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AN INVESTIGATION OF THE HARDENING OF ASPHALT RECOVERED FROM PAVEMENTS OF VARIOUS AGES

A THESIS

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ASPHALT RECOVERED FROM PAVEMENTS OF VARIOUS AGES

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF ILLUSTRATIONS

LIST OF ILLUSTRATIONS (Continued)

SUMMARY

Hardening of the asphalt cement binder is one of the primary causes of bituminous roadway pavement failure. The changes that occur in asphalt during service are not well understood but are due to a combination of physical, chemical, colloidal, and rheological properties.

The hardening process has been studied several times using either actual pavement cores or methods of artificial aging. Empirical tests, such as penetration and ductility, have been developed to measure the changes during hardening. However, to provide a more fundamental approach to the study of asphalt, the sliding plate microviscometer was developed, providing an absolute measure of the viscosity of asphalt. A more recent approach makes use of an infrared spectrophotometer.

The purpose of this study was to determine how the hardening of asphalt in actual pavement cores varied with depth below the pavement surface. Each core, 1 - 13 years old, was sliced in one-fourth inch layers parallel to the pavement surface, and the asphalt from each layer was recovered by the Abson Technique. The viscosity was determined and related to depth, age of pavement, and original viscosity. The spectrophotometer was used to give some insight into the chemical changes occurring in the top one-half inch.

The results show that there is an increase of approximately 50 percent in the viscosity of asphalt recovered from the top one-fourth inch over asphalt recovered from the next lower slice. There is a very

thin film at the pavement surface which has a higher viscosity than the average viscosity in the top one-fourth inch layer.

Increases in viscosity with age are more apparent in the top one-half inch than at lower depths; there is only a small change in viscosity at lower depths, except for an initial increase occurring before or during placing.

In the upper one-half inch, asphalts with lower viscosities were found to increase in viscosity more rapidly than asphalts with high original viscosities.

Hardening due to aging was indicated by the infrared spectrum at wavelengths of 2.91, 5.88, and 9.71 microns, but the 5.88 micron wavelength gives the best indication of changes in hardening with depth.

CHAPTER I

INTRODUCTION

One of the primary causes of a roadway pavement surface failure is hardening of the asphalt cement binder. Excessive hardening due to any cause is undesirable because it may reduce adhesiveness and durability in service. Ideally, a binder should be sufficiently fluid to permit mixing with the aggregate, adhere well to the aggregate in the presence of water, and not become brittle with aging (1).*

The changes that occur in asphalt are not well known but are due to a number of causes involving the complex composition of asphalt. Researchers have found that it is both a chemical and a physical problem. Changes in colloidal and rheological properties are also thought to be relevant (2). Some have found that hardening with time is related to asphalt source, method and degree of mixing, and method of placing.

Traxler lists fifteen effects which cause changes in asphalt characteristics (3). Most important are:

1. "Oxidation in the absence of sunlight is probably the most important effect influencing the hardening and loss of binding power of asphaltic cements. It occurs continuously when the bitumen is in contact with air and the rate of oxidation is dependent upon the temperature."

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*Numbers in parentheses refer to similarly numbered references in List of References at end of thesis.

2. Photooxidation under direct sunlight severely affects a very thin layer of asphalt on the surface and probably is the cause of much of the deterioration of the wearing surface.

3. Volatilization often is of considerable importance during the construction of hot mix pavements. However, during the service life of the pavement it may be of minor importance. The viscosity of the asphalt and the time and temperature of exposure affect volatilization.

4. Polymerization, the hardening of an organic material caused by application of heat, affects hardening depending on temperature, time, and composition of the bitumen.

5. Age hardening is a thixotropic effect occurring well below the softening point. It is evidenced by a structure development within the asphalt, part of which is destroyed by heat of working. It is dependent upon the composition of the asphalt.

6. Water, especially in conjunction with air and sunlight, affects asphalt either as a catalyst for many chemical reactions or through the formation of many products, both water soluble and insoluble.

Other factors include: Photooxidation under reflected light, photochemical action of direct sunlight, photochemical action of reflected (polarized) light, exudation of oil, absorption of oil by solids, adsorption of asphaltic components at a solid surface, catalytic effects, and microbiological deterioration. It should be noted that all of the above are important, and it is impossible to assign a definite order of importance. Time, temperature, and thickness of film are factors in all the effects listed.

In studying the problem of hardening, there are two approaches

that may be taken. The first is a study of asphalt pavements in actual service, which has been used many times. In most cases accurate information can be obtained on the original asphalt and the conditions of the pavement while in service. Several factors, however, have limited the use of this method. Long periods of time are necessary to evaluate the service, cost of such experiments is high, and many uncontrollable factors which have little effect on the asphalts are encountered. Usually, these uncontrollable factors are interrelated, making it difficult to determine the effect of any one.

Even with these disadvantages there have been large scale experiments conducted which yielded valuable information (3).

As early as 1935 researchers recognized the disadvantages of natural aging and developed methods of artificial aging. Using various methods they were able to simulate the natural aging phenomena. These methods partially overcame the disadvantages of cost, time, and interrelationship of variables encountered in nature. Usually the methods attempted to accelerate the weathering process through cycles of light, water spray, and chilling. Data indicated that these efforts were partially successful.

Modern methods used in the laboratory to age asphalt are high temperature, ultraviolet light, chemical oxidation agents, and oxidation in solution under pressure.

To evaluate the effects of aging, various empirical tests, such as penetration, ductility, softening point, and various relative viscosity tests, have been developed to record changes in asphalt properties. The empirical nature and dissimilarity of these tests have greatly limited their use, especially for comparative purposes.

Schweyer (4) states:

> One of the most striking examples of the lack of scientific approach in asphalt technology is the continual use of empirical tests such as penetration ductility, and others. The data from such tests with few exceptions are difficult to correlate quantitatively with the performance of asphalts in service.

However, to provide a more fundamental approach to the study of asphalt, the sliding plate microviscometer was developed providing a measure of the rheologic behavior of asphalts. It has the advantage of permitting determination of absolute viscosity of asphalts in thin films.

Schweyer and Bransford (5) define viscosity:

> When a plane one square centimeter in area requires a force of one dyne to move it at a velocity of one centimeter per second with respect to a second plane one centimeter distant, then the fluid between the planes has a viscosity of one poise equal one dyne-second per square centimeter.

Mathematically, viscosity is a proportionality constant which relates the known values of force per unit area, F, to shear rate, S. If

$$F = nS$$

were absolutely true (n constant) a straight line plot would result when S was plotted as a function of F. In this case the material is called Newtonian. But due to complex flow properties this is not always true and the material is non-Newtonian. Using logarithmic paper the plots appear as straight lines and are represented by the equation

$$M = F/S^{c}$$

where M is a constant for the plot and c is the slope of a logarithmic plot and measures the degree of complex flow. This equation may apply to

both Newtonian and non-Newtonian materials as c equals one for Newtonian materials.

A more recent approach to the study of asphalt makes use of an infrared spectrophotometer. Hilliard and Srail (6) define spectrophotometry as "the science which includes the measurement of the relative intensity of transmitted or reflected radiant energy." Furthermore, "Infrared spectrophotometry discloses information regarding the vibration of chemical molecules. This depends on the masses of adjacent atoms and the distance between them." Infrared spectrophotometry detects the presence of groups of atoms, not individual elements. These atoms vibrate at frequencies characteristic of the molecular combinations present. A sample placed in the infrared beam will absorb infrared energy at frequencies characteristic of the molecule. By varying the frequency, a complete infrared spectrum may be obtained. This spectrum can indicate the presence of certain functional groups, such as carbonyl or hydroxyl, or the change in such groups due to aging or exposure.

CHAPTER II

LITERATURE SURVEY

Asphalt Variation with Depth

In the study of asphalt durability there have been many studies of the causes and effects of hardening. However, few studies have dealt with the aging of thin asphalt layers parallel to the surface of the pavement.

Pauls and Halstead (7) found that after a 19 year period there was a considerable variation in the hardening of asphalt within the same core. Asphalt near the surface hardened to a greater extent and lost a larger percentage of ductility than did the material in the center or bottom of the pavement. Both top and center samples showed more hardening than did the bottom. Very little change was indicated in the penetration of asphalt in the bottom quarter inch of the 19 year old sample as compared to a sample extracted immediately after mixing. Only one sample was reported, making definite conclusions impossible.

Simpson, Griffin, and Miles (8) found that, in general, the asphalt in the top one-fourth inch of pavement had a higher viscosity than the rest of the pavement, including both the surface and base. They used the microviscometer to study 32 and 35 month old cores taken from the Zaca-Wigmore Experimental Road in California. At depths lower than one-half inch, within the surface course, there was less change than in the top half inch. Higher viscosities were sometimes encountered in

the top of the base course indicating that appreciable hardening occurred between the laying of base and surface courses. Also, they found a general agreement between air void content of the compacted mix and viscosity: cores with higher air void content had higher viscosities at equal depths.

Asphalt Aging

Numerous studies have been made concerning asphalt aging. Neppe (9) and the Highway Research Board (10) have published bibliographies which together list about 300 publications. Only a few of the more important can be listed here.

Hubbard and Reeve (11) made what was probably the first study of aging in 1913 by exposing thin films of asphalt for one year. They observed a 75 percent decrease in penetration in this period. Traxler and Schweyer (12) in 1936 established the first conclusive evidence that viscosity increased with time, temperature held constant.

Brannon (13) studied actual pavements in 1937 and found that decrease in penetration varied from 22 percent at 4 months to 47 percent at 30 months. As much as 24 percent was found to occur before or during placement. Identical asphalts decreased in penetration by different amounts when placed in different areas.

White (14) found that asphalt content is the greatest single factor determining the amount of drop in penetration of asphalt with service. Asphalt in cutback asphalt wearing surfaces hardens in about six years to the point of incipient raveling. Pauls and Welborn (15) concluded that an increase in hardening as indicated by decrease in penetration is accompanied by changes in other properties, such as an increase in softening point and a decrease in ductility.

Brown, Sparks, and Larsen (16) developed an equation to relate early changes in ductility, softening point, or penetration to ultimate pavement performance:

$$T/\Delta Y = a + bT$$

where T is time since paving (yr), Y is softening point, ductility, or penetration, and a and b are empirically determined constants. When Y is plotted as a function of T the hyperbolic form appears with asymptotic values reached at about nine to ten years.

Parr and Serafin (17) found that penetration of asphalt extracted from cores decreased up to 17 months and then remained relatively constant or increased slightly at ages of 29, 40, and 52 months. Penetration was found to be greater under the center of the traffic lane than under the wheel paths. Simpson, Griffin, and Miles (8) substantiated this finding by noting that most hardening occurred in the first 16 to 20 months and then decreased considerably.

Skidmore and Abson (18) studied hardening during manufacture. They pointed out that even under good control during manufacture, a 10 to 20 point decrease in penetration may be expected. Lang and Thomas (19) reported an average of 9.1 percent loss in penetration of 50 - 60 penetration asphalts immediately after mixing.

Bissett (20) recovered asphalt from pavements and tested them for ductility, penetration, and softening point. He found a 28 percent decrease in penetration during mixing and placing. He concluded that early loss of penetration and ductility, primarily ductility, causes cracking of the pavement surface.

Spectrophotometer Use

The literature on the use of the spectrophotometer in asphalt research is limited to a few publications. It has not been definitely established which infrared wavelengths indicate the various possible changes in asphalt. In fact, Schweyer (21) found that asphalts apparently could not be characterized specifically by their spectral absorption. He compared this to a concept presenting the idea that only gross absorption bands may be used in complex mixtures such as asphalt since there are compensating absorption effects.

Beitchman (22), in a study of 28 asphalts, noted similar absorption characteristics in the infrared spectra of asphalts from widely different sources. There was a relationship between the transmittance of several absorption bands and durability. The bands observed were hydroxyl, $-CH_2-$, C-O, $C-CH_3$, carbonyl, $-(CH_2)_4-$, and aromatic rings. The carbonyl band was the most important, but the hydroxyl and C-O bands also showed some changes.

The change in infrared absorption at 5.88 microns with time of exposure to carbon arc radiation was used by Wright and Campbell (23) to study oxidation. They found an inverse relationship between durability and rate of oxidation. Only the carbonyl band, 5.88 microns, was used; as it is a sharp absorption band free from interference in the infrared and more accurate than the O-H, 2.91 micron, C-O, or 9.71 micron bands. After an induction period there was a steady rate of increase in oxidation.

Greenfeld and Wright (24) used the carbonyl band to measure the changes in absorbance as a measure of oxidation of roofing asphalts.

It was found that durability varied inversely with carbonyl index for unmodified asphalts. While low values of carbonyl index are indicative of good durability, high values may or may not indicate poor durability. The hydroxyl and C-O absorption bands both showed a decreasing of infrared transmittance with longer periods of oxidation. However, the changes in transmittance at these bands were too small to accurately indicate differences.

The oxidation rates of two air-blown asphalts were studied by Wright, Campbell, and Fridinger (25) using the infrared absorption in the carbonyl band. They found an increase in oxidation rate with intensity of carbon arc and time of exposure at constant temperature. Similar changes in absorption were also indicated at the hydroxyl band and carbon-oxygen-carbon band.

The carbonyl index was used by Campbell, Wright, and Bowman (26) in their work on the effect of temperature and humidity on oxidation. They noted an inverse relationship between carbonyl index and temperature and relative humidity.

CHAPTER III

PROCEDURE

The asphalt samples used in this project were obtained from existing pavements in Georgia through the cooperation of the Georgia State Highway Department. In accordance with the objectives of the project, asphalt samples were obtained by extraction and recovery from cores taken from existing pavements. These cores are well representative of ages from 4 months to 12 years. A summary of projects and asphalt data appears in Table 1. All cores were obtained from locations near Atlanta, Georgia, with the exception of numbers one and two, which came from southern Georgia. To the author's knowledge no special conditions were encountered during placing or service life which would affect the results.

Recovery

Two six inch diameter cores were obtained from each project. These cores were transported to the laboratory, placed in water, and covered to prevent further aging by air or light. Balls of steel wool were placed in the water to lessen the possibility of oxidation by dissolved oxygen in the water.

In order, each core was removed from water and the surface course sliced into one-quarter inch slices with a diamond blade saw. Care was taken not to include the binder or underlying layers. The top layer was placed in the oven while the other slices were returned to the water

Table 1. Sample Description

Sample Number	Project	Location	Date Placed	Age (mo)	Asphalt Grade	Specific Gravity	Original Penetration	Original Viscosity* (megapoises)
1	F-007-2(N) ct 1	Thomasville-Quitman Rd Brooks Co., Ga.	Mar. 1965	4	AC-6	1.028	67	2.60*
2	PR-1421-B(1)	Excelsior Rd Tift Co., Ga.	Jan. 1965	6	AC-6	1.026	66	2.69*
3	RA 15-8(5)	Decatur-Tucker Rd DeKalb Co., Ga.	July 1964	9	AC-6	1.032	64	2.82*
4	I-20-1(4) ct 1	I-20 West Fulton Co., Ga.	Sept. 1964	10	AC-6	1.029	71	2.36
5		Ga. Tech Electrical Engr. Parking Lot	Sept. 1964	10	AC-6	1.038	69	2.43
6	I-20-1(4) ct 1	I-20 West Fulton Co., Ga.	Sept. 1964	10	AC-6	1.046	66	2.72
7	F-074-2(4)	W. Fayetteville Rd College Park, Ga.	Aug. 1964	11	AC-6	1.029	79	1.94
8	US-1394(2)	N. Druid Hills Rd Atlanta, Ga.	July 1963	24	AC-6	1.041	63	2.90*
9	SAP 719A(9)	College Ave. Atlanta, Ga.	June 1961	47	AC-8	1.040	95	1.43*
10	DS-0696(2)	Lawrenceville-Duluth DeKalb Co., Ga.	Aug. 1959	70	AC-8	1.026	94	1.46*
11	F-074-2(4)	S.R. 85 North of Fayetteville, Ga.	June 1956	109	AC-8	1.029	96	1.41*
12	SAP 719A(5)	East Lake Dr Atlanta, Ga.	Oct.-Nov. 1954	126	AC-8	1.032	93	1.48*
13	SAP 1083 c(1)	Atlanta-Buford Rd DeKalb Co., Ga.	Feb. 1954	135	AC-8	1.032	94	1.46*
14	SAP 1214 B(3)	Stone Mt.-Tucker Rd DeKalb Co., Ga.	Oct. 1952	151	AC-8	1.042	90	1.57*

*Original viscosity obtained from empirical equation: Abs. Visc. = $3591.3(\text{Pen})^{-1.719}$
See Reference 27

for later use.

After drying for 20 minutes at 250 degrees F, the sample was broken into small pieces and returned to the oven for ten minutes. This loosened the asphalt from the aggregate and permitted placement in the extraction bowl. An analytical reagent grade benzene was used to extract the asphalt. A total of 240 milliliters of benzene was used in three steps on the approximately 275 gram sample. The asphalt - benzene solution was then centrifuged at 770 times gravity for 30 minutes to remove dust and other suspended matter.

The Abson Technique, ASTM D-1856-63, was used with slight modification to recover the asphalt. This modification was the use of a 275 gram sample since it was not possible to obtain a 1200 gram sample from the one-quarter inch slice. This necessitated extreme care in the distillation to prevent oxidation or overheating.

A study was made to determine the influence of sample size and of operator on viscosity. The percent difference between the viscosities determined from a 1200 gram sample and a 275 gram sample was only about six percent. The difference between operators was about eight percent. These were considered to be within satisfactory limits and not to adversely affect results.

The apparatus used is the same as in ASTM D-1856-63 and is shown diagrammatically in Figure 1. In accordance with standard procedure, all extraction distillations were completed in less than eight hours. The recovered asphalt samples were placed in sealed tin boxes until they were tested.

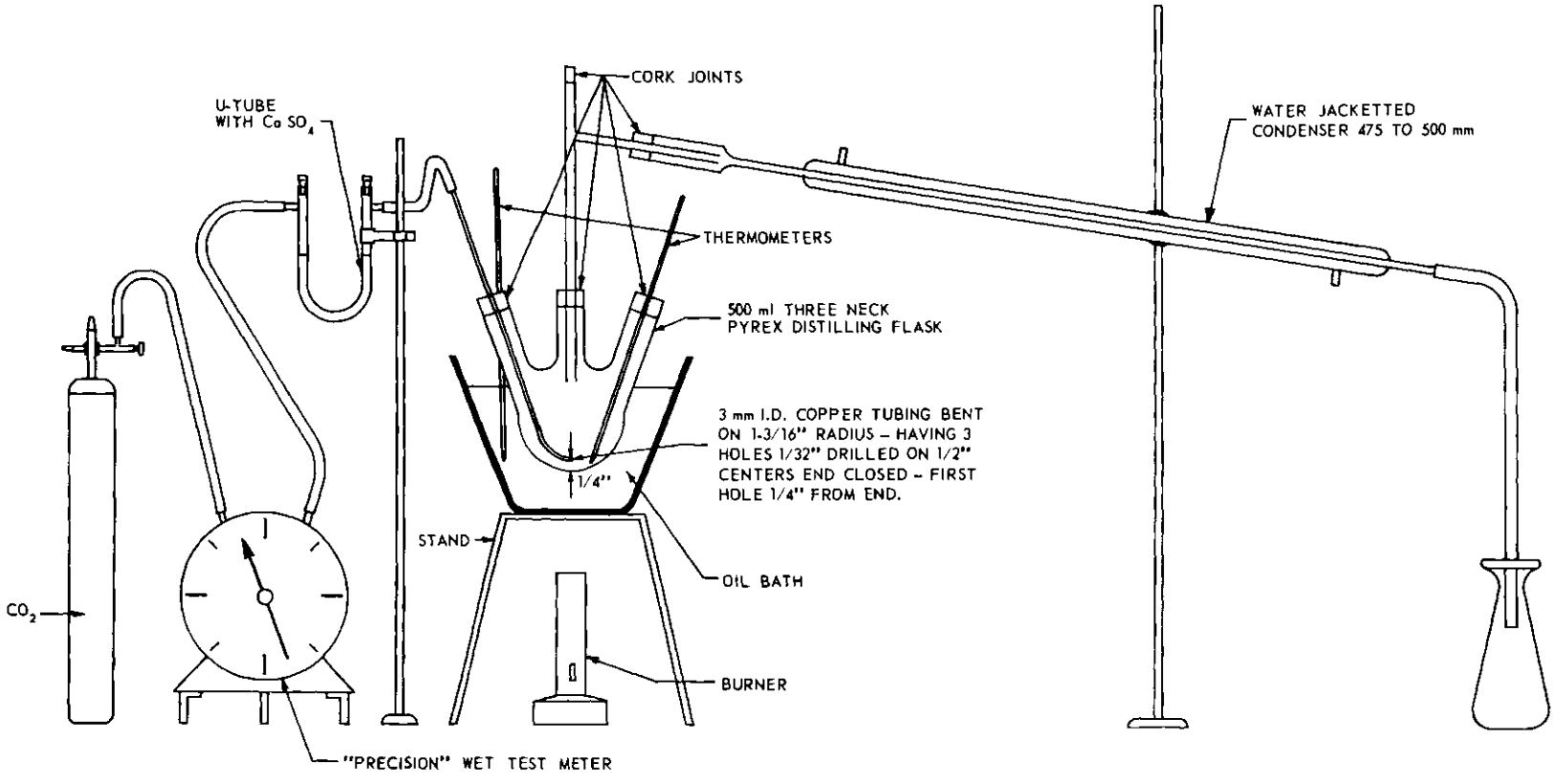

Figure 1. Distillation Equipment.

Viscosity

Viscosity testing was performed with the sliding plate microviscometer developed by Shell Development Company. It is shown in Figure 2. The procedure was relatively simple, but some time was required to reach a degree of skill in making the plates.

The asphalt sample was heated in the oven at 250 degrees F for five to ten minutes until it was slightly fluid. A set of glass plates was also heated for three to four minutes. Then both sample and plates were removed and a drop of hot asphalt was placed on one of the plates. The other plate was immediately placed on top and the two plates pressed together until a uniform film, approximately 50 to 60 microns thick, was obtained. The excess asphalt was cleaned from the plates, plates and sample weighed, and film thickness calculated from asphalt weight and specific gravity. An hour was required for the plates to cool before viscosity was determined. Duplicate sets of plates were prepared for each sample.

To begin the viscosity determination, one of the plates was clamped in the viscometer frame and the other in a movable clamp through which the loads were transmitted. The desired load, up to 10,000 grams, was applied through a simple balance beam. At least three, and usually four, loads were required to get several shear rates to interpolate accurately to 0.05 reciprocal seconds. A shear rate of 0.05 reciprocal seconds at 77 degrees F was used in this research.

Spectrophotometer

A spectrophotometer analysis was made of the upper two layers of

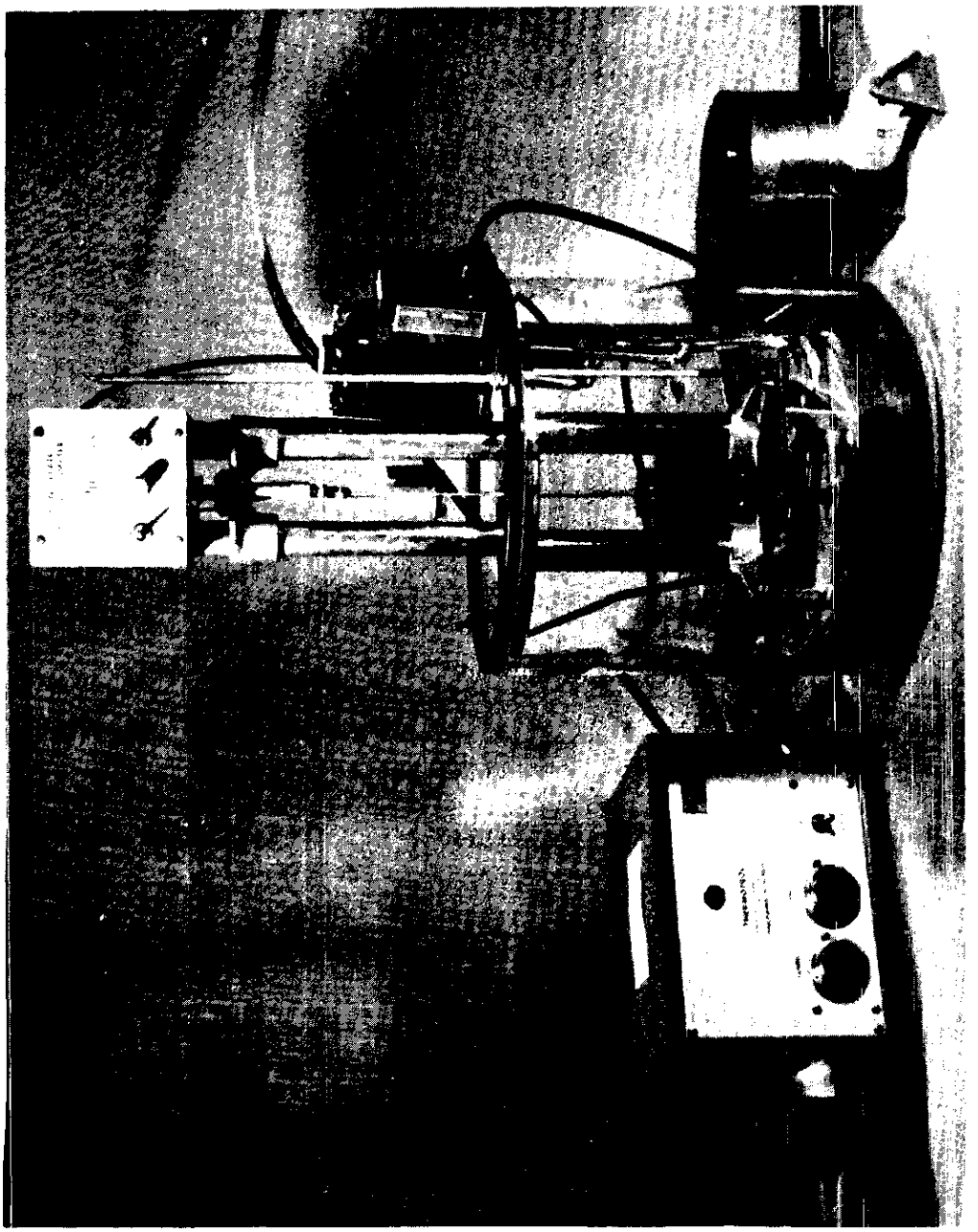

Figure 2. Sliding Plate Microviscometer.

six selected cores. The procedure for this testing was developed by personnel of Georgia Tech Research Project A-711.

The spectrophotometer plates are similar in appearance to the microviscometer plates but are made of sodium chloride. They are approximately four by two centimeters. An asphalt film thickness of 75 microns with an allowable variance of 5 microns was chosen for this study.

A film former, shown in Figure 3, was used so that a constant thickness could be obtained. The technique used to make these plates requires preheating the film former, sodium chloride plates, and asphalt sample to about 200 degrees F. A drop of asphalt was placed on one of the plates and the other plate set on top. Both plates were than placed in the film former, which then correctly adjusted pressed the plates together so that a film thickness of about 75 microns was formed. Several trials were required to achieve the desired thickness; occasionally the film was pressed too thin. In this case the plates had to be cleaned and the procedure repeated.

After removing the excess asphalt, the plates were placed in the spectrophotometer and the infrared spectrum recorded. A Beckman IR-8 spectrophotometer, shown in Figure 4, was used in this research.

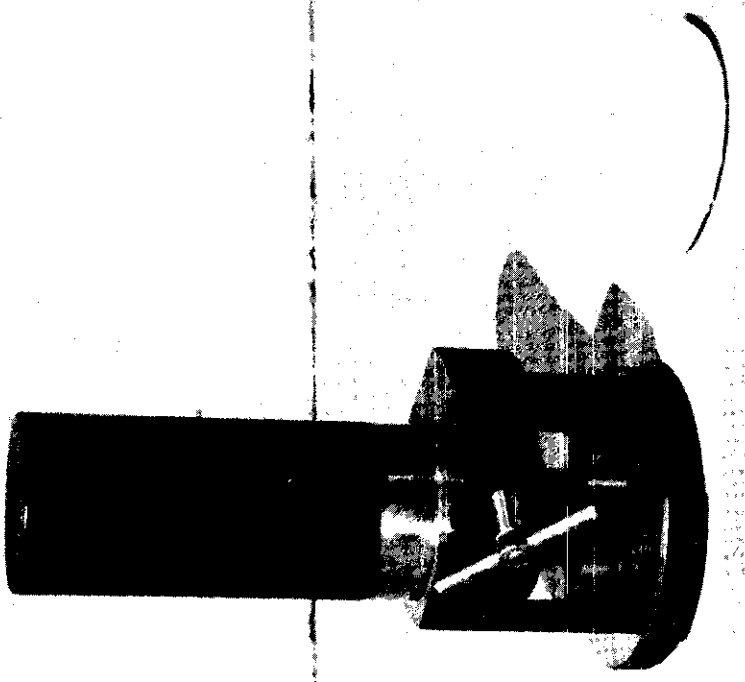

Figure 3. Film Former.

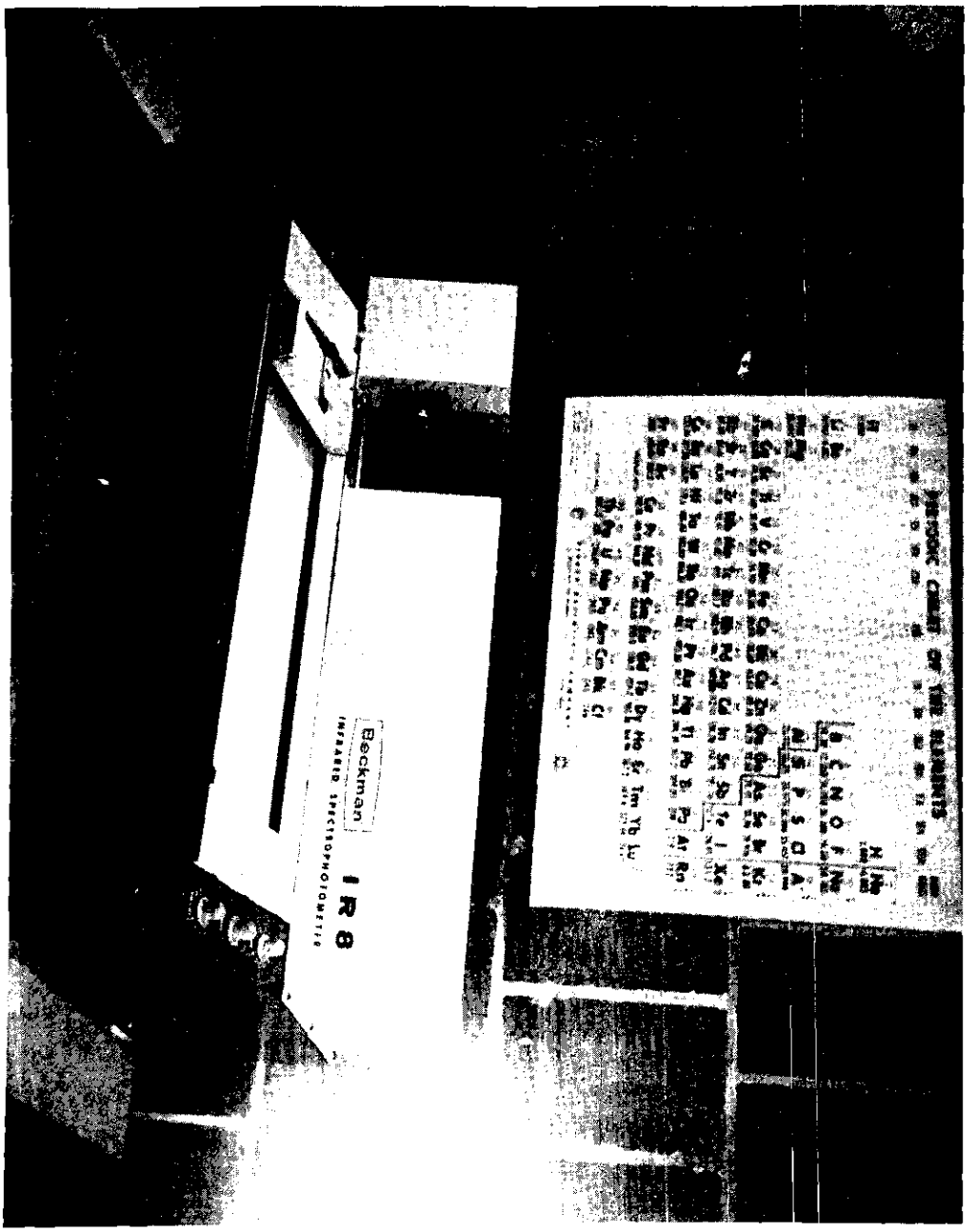

Figure 4. Beckman IR-8 Spectrophotometer.

CHAPTER IV

INSTRUMENTATION AND EQUIPMENT

Extractor

A Dulin Rotarex model 11170 extractor manufactured by the Braun Corporation was used in this experiment.

Centrifuge

An International model C-50 centrifuge capable of handling two eight-ounce wide mouth bottles at 770 times gravity was used.

Distillation Assembly

The distillation assembly is shown in Figure 1. It is the standard apparatus described in ASTM D-1856-63 using the oil bath.

Sliding Plate Microviscometer

The microviscometer used was developed by Shell Development Company and is shown in Figure 2. It is capable of measuring the absolute viscosity between 100 and 100 billion poises.

Spectrophotometer

This instrument was a Beckman IR-8 spectrophotometer which transmits infrared light over a range of 2.5 to 16 microns wavelength. It is shown in Figure 4.

Film Former

The film former used is shown in Figure 3.

Sodium Chloride Plates

These plates of clear sodium chloride, two centimeters by four centimeters, were used in the spectrophotometer. They are shown beside the film former in Figure 3.

CHAPTER V

DISCUSSION OF RESULTS

Viscosity Study

The results of the 14 asphalt viscosity determinations are shown in Table 2. The one-fourth inch layers are referred to as layers A, B, C, D, and E in succession beginning at the pavement surface proceeding downward. Since the diamond blade used in cutting the slices was one-eight inch thick, the depths of each slice are not multiples of one-fourth inch. The actual depths are as follows:

Layer	Actual Depth
A	0 - 1/4"
B	3/8 - 5/8"
C	3/4 - 1"
D	1-1/8 - 1-3/8"
E	1-1/2 - 1-3/4"

It will be noted that samples 1 through 8 are 60 - 70 penetration grade and samples 9 - 14 are 85 - 100 penetration grade asphalt cement. Due to a general change from AC-8 to AC-6 asphalt by the Georgia Highway Department in 1963, it was not possible to obtain recent samples of AC-8 asphalt. For this reason the viscosity data for the AC-6 and AC-8 samples will be analyzed separately as well as a unit. Average viscosity results are shown for all 14 samples and for the AC-6 and AC-8 samples respectively.

Viscosity Versus Depth

Figure 5 shows the average viscosity of all 14 samples at each

Table 2. Absolute Viscosity Results*

Sample Number	1	2	3	4	5	6	7	8	Ave. AC-6	9	10	11	12	13	14	Ave. AC-8	Ave. of 5**	Overall Ave.
Age (mo)	4	6	9	10	10	10	11	24		47	70	109	126	135	151			
Layer A	22.8	24.4	6.4	22.8	17.5	22.4	19.8	21.4		20.4	20.3	31.8	22.1	11.4	56.0			
	23.2	24.4	6.6	24.4	18.4	23.1	21.5	20.9		21.4	24.1	29.5	22.8	11.2	58.5			
									20.1							27.7	22.6	23.4
Layer B	14.7	13.6	23.0	13.3	13.2	13.9	14.2	12.0		7.7	17.5	11.9	14.1	12.6	30.0			
	14.9	13.2	23.9	13.1	11.7	13.4	15.1	13.1		7.4	18.6	12.6	15.2	12.3	30.6			
									14.8							15.9	13.3	15.3
Layer C	14.9	14.4	25.3	13.3	10.6	13.7	12.7	10.7		5.7	15.1	9.2	14.4	10.9	-			
	15.7	14.6	25.6	14.3	11.1	13.9	13.1	9.9		5.9	16.1	9.7	13.9	11.3	-			
									14.6							11.2	12.8	13.3
Layer D	14.8	14.4	23.6	12.5	-	12.5	12.2	11.7		3.4	13.3	7.3	-	9.6	-			
	15.3	14.5	24.7	12.5	-	12.7	14.0	10.9		3.3	13.7	7.1	-	9.8	-			
									14.7							8.4	11.8	12.4
Layer E	12.5	12.8	20.6	-	-	13.3	-	-		-	-	6.6	-	6.9	-			
	12.6	13.5	21.8	-	-	13.5	-	-		-	-	6.1	-	7.2	-			
									15.1							6.8	10.6	12.3
Ave.	16.1	15.9	20.2	15.8	13.8	15.4	15.3	13.8		9.5	11.7	13.2	17.1	10.3	43.8			

*All values megapoises

**Average of samples 1, 2, 6, 11, and 13.

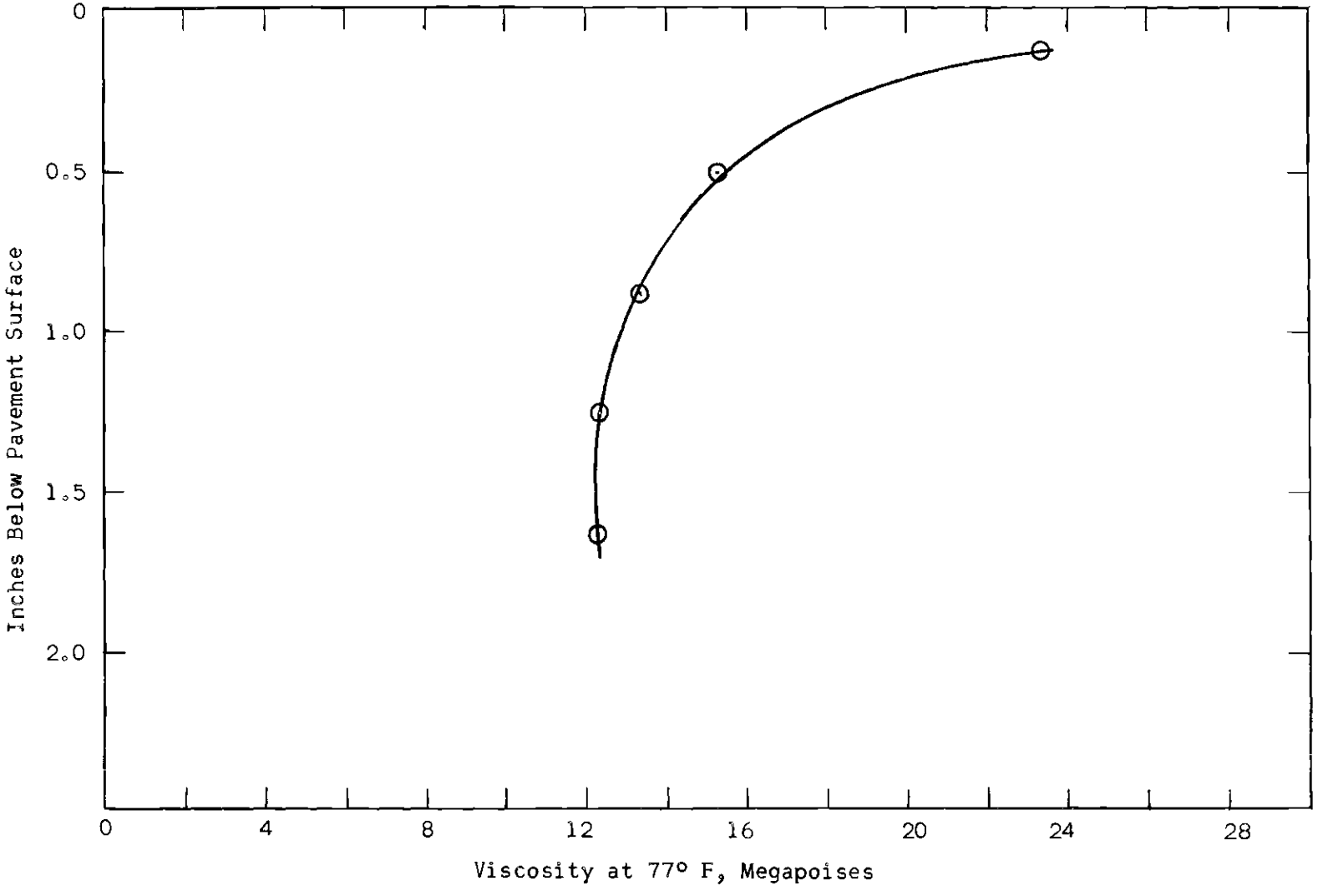

Figure 5. Average Viscosity of Samples 1 - 14 Versus Depth.

layer. In general, it is apparent that the greatest change in viscosity occurs in the top half-inch. The average viscosity in layer A is 23.4 megapoises and the average in layer B is 15.3 megapoises. This shows the average viscosity of layer A is about 50 percent greater than layer B. The differences between layers B and C, C and D, and D and E, respectively are 11 percent, 7 percent, and 1 percent.

To better interpret these results a computer program was used to make an analysis of variance on the relative viscosities. Relative viscosity is defined as the ratio of the viscosity of the hardened sample divided by the original viscosity. It is a measure of the hardening of the asphalt. A high value of relative viscosity indicates much hardening and a low value indicates little hardening and, thus, probable superior pavement durability in service. Relative viscosity was used rather than absolute viscosity to remove the effect of initial viscosity so that only change in viscosity would be tested. Table 3 shows the original viscosity of each layer and the relative viscosity of each extracted sample.

The analysis indicated a significant effect at the 0.1 percent level due to age. It also showed that there was a significant effect at the 0.1 percent level due to depth.

To further interpret this data, Duncan's Multiple Range Test was used to indicate which layers were the sources of the difference with depth. It showed a significant difference between layers A and B at the 1.0 percent level and between layers B and C at the 5.0 percent level. No difference was found at the 5.0 percent level among the three lower layers.

Table 3. Relative Viscosity Results

Sample Number	1	2	3	4	5	6	7	8	Ave. AC-6	9	10	11	12	13	14	Ave. AC-8	Ave. of 5*	Overall Ave.
Age(mo)	4	6	9	10	10	10	11	24		47	70	109	126	135	151			
Original Viscosity (Mega-poises)	2.60	2.69	2.82	2.36	2.43	2.72	1.94	2.90		1.43	1.46	1.41	1.48	1.46	1.57			
Layer A	8.8	9.1	2.3	9.7	7.2	9.0	10.2	7.4		14.3	15.8	22.6	14.9	7.7	35.7			
	8.9	9.1	2.3	10.3	7.6	8.5	11.1	7.2		15.1	16.5	20.9	15.4	7.8	37.3			
									8.0							18.7	11.2	12.6
Layer B	5.7	5.1	8.2	5.6	5.4	5.1	7.3	4.1		5.4	12.2	8.4	9.5	8.6	19.1			
	5.7	4.9	8.4	5.5	4.8	4.9	7.8	4.5		5.2	12.5	8.9	10.3	8.4	19.5			
									5.9							10.7	6.6	7.9
Layer C	5.7	5.4	9.0	5.6	4.4	5.0	6.6	3.7		4.1	10.6	6.5	9.7	7.5	-			
	6.0	5.4	9.0	6.1	4.5	5.1	6.8	3.4		4.2	10.9	6.9	9.4	7.7	-			
									5.7							7.7	6.1	6.5
Layer D	5.7	5.4	8.4	5.3	-	4.6	6.3	4.0		2.4	9.3	5.2	-	6.6	-			
	5.9	5.4	8.7	5.3	-	4.7	7.2	3.8		2.3	9.3	5.1	-	7.0	-			
									5.8							5.9	5.5	5.8
Layer E	4.8	4.8	7.3	-	-	4.9	-	-		-	-	4.7	-	4.9	-			
	4.9	5.0	7.7	-	-	5.0	-	-		-	-	4.7	-	4.9	-			
									5.5							4.8	4.9	5.3
Ave.	6.2	5.9	7.1	6.7	5.7	6.7	7.9	4.8		6.6	12.1	9.4	11.5	7.1	27.9			

*Average of samples 1, 2, 6, 11 and 13.

The previous paragraphs clearly indicate that the major increase in viscosity is in layer A. The question now arises as to how the viscosity varies within layer A itself. To answer this question three sample numbers, 8, 10, and 12, were selected for further study. Taking the duplicate cores of these samples, the top 1/16 inch was shaved off with the saw. A one-fourth inch layer (actual depth 1/16 - 5/16 inch and designated "A_s") was then sliced and the viscosity determined. The results are shown in Table 4.

The average viscosity of these three A_s samples was 16.6 megapoises, whereas the average in layer A of the three original cores was 22.4 and in layer B was 15.1. This represents a 25.8 percent decrease in viscosity from layer A upon the removal of the top one-sixteenth inch. However, it is only ten percent greater than the original viscosity of layer B. A straight line interpolation between the original viscosities at the average depth of layer A, 0.125 inch, and the average depth of layer B, 0.50 inch, would give an expected viscosity of 21.0 megapoises at the average depth of A_s, 0.1875 inch. See Figure 6. Since the recorded viscosity is only 79 percent of this value, it is apparent that most of the hardening occurs in a very thin layer (less than 0.1875 inch) immediately below the pavement surface.

Figures 7 and 8 show the average viscosity as a function of depth for the AC-8 and AC-6 samples, respectively. It should be noted that the AC-8 samples are all 47 months or more old, and the AC-6 are all 24 months or less old.

For the AC-8 samples the curve appears very similar to Figure 5. The increase in layer A, 27.7 megapoises, over layer B, 15.9 megapoises,

Table 4. Viscosity in Top One-half Inch

Layer	Average Depth (inch)	Sample Number 8	10	12	Average
A	0.125	21.4 20.9	23.0 24.1	22.1 22.8	22.4
A_s	0.188	14.2 13.5	14.3 15.9	17.0 16.5	16.6
B	0.500	12.0 13.1	17.5 18.6	14.1 15.2	15.1

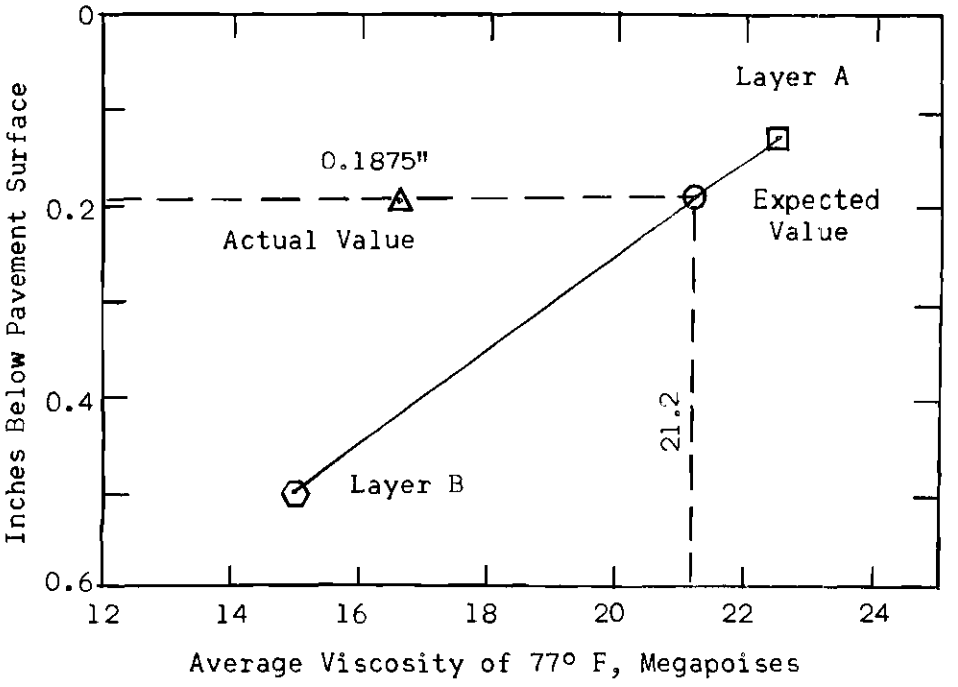

Figure 6. Average Viscosity Versus Depth in Top One-half Inch.

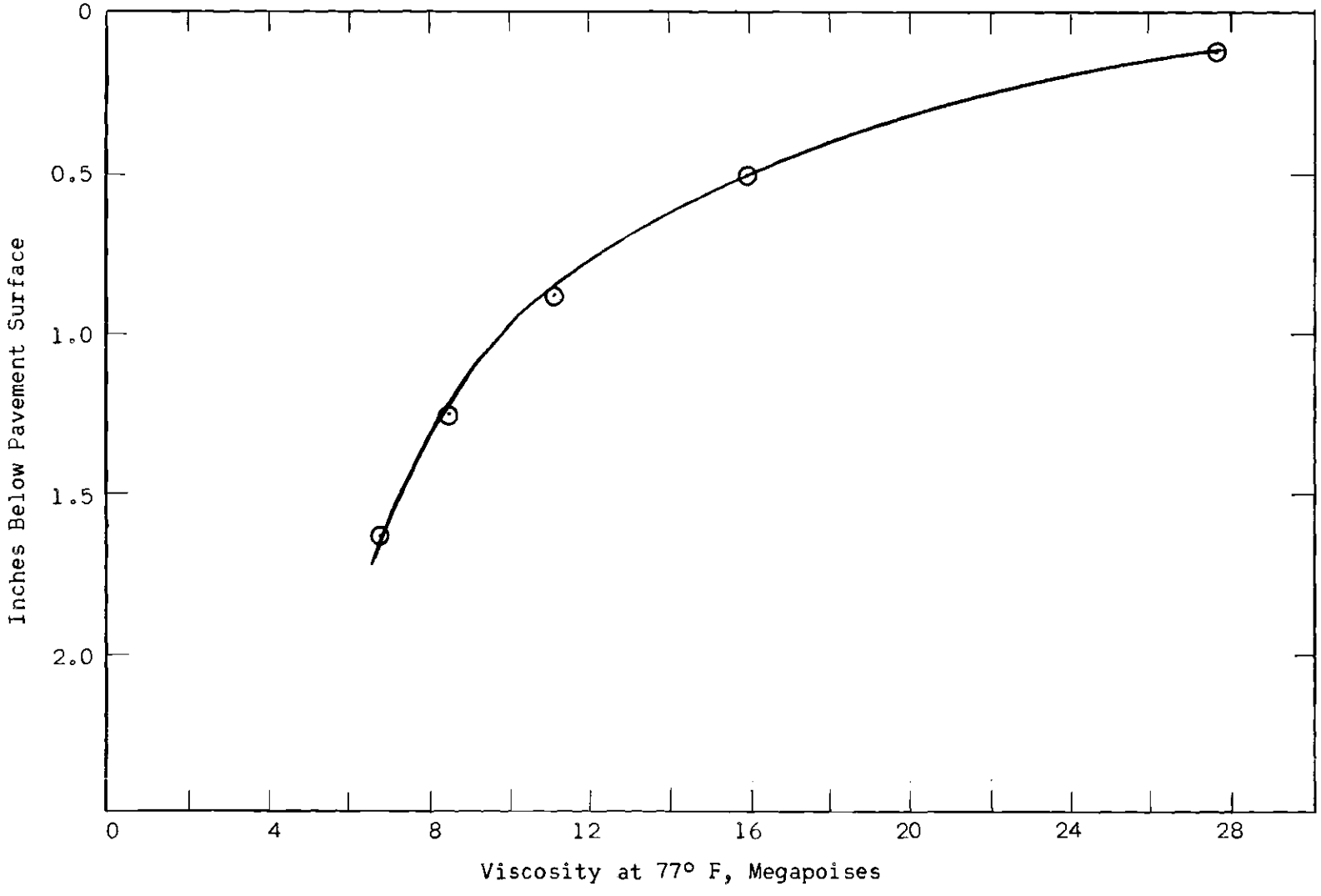

Figure 7. Average Viscosity of AC-8 Samples Versus Depth.

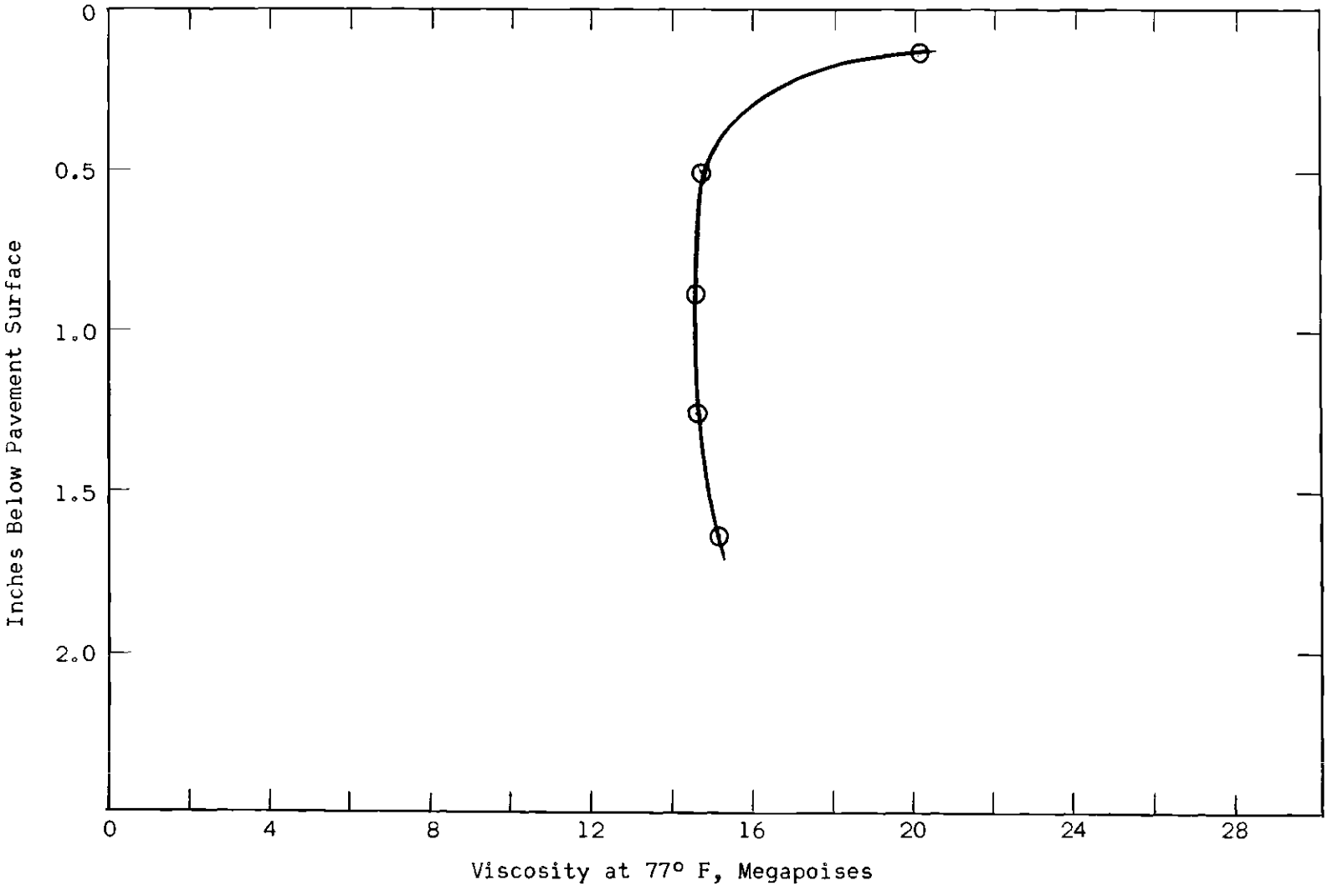

Figure 8. Average Viscosity of AC-6 Samples Versus Depth.

was about 75 percent. Percent differences of 42, 33, and 24 were found between layers B and C, C and D, and D and E, respectively. In the analysis of variance, a significant difference was found between ages and also between depths at the 0.1 percent level. Duncan's Multiple Range Test showed that each layer was significantly different from all other levels at the 1.0 percent level.

The curve of the AC-6 samples shows that the viscosity in the top quarter inch is about 36 percent greater than that in layer B. But the difference in viscosity of layers B through E is less than three percent in all cases. In the analysis of variance, the relative viscosities at different depths and different ages were found to be significantly different at the 0.1 percent level. Duncan's Multiple Range Test showed a significant difference between layers A and B at the 1.0 percent level but no significant difference between any other two consecutive layers at the 5.0 percent level.

Considering Figures 5, 7, and 8 together it appears that as a unit there is a higher viscosity in the top quarter inch than at greater depths below the pavement surface. As depth becomes greater the percent difference between adjacent layers is less. The older AC-8 samples show essentially the same results but the AC-6 samples by themselves indicate that the greatest change in viscosity occurs only in the top quarter inch and that in the first two years there is no appreciable change in viscosity with depth except in layer A. The viscosity increase in the lower layers is approximately uniform indicating that it probably occurred during mixing, transporting, or placing.

The effect of age will be discussed more completely later.

From Table 2 it can be seen that all samples did not have the full depth of five layers; consequently any individual value has more relative weight on the average than a value at a higher layer of the same sample. For this reason samples 1, 2, 6, 11, and 13, each having five layers, were analyzed separately. Sample no. 3 was not included because of the low result found in layer A. A graph of average viscosity versus depth is shown as Figure 9. It shows a 70 percent increase in viscosity of layer A over layer B. The difference between other layers is from four to eleven percent.

An analysis of variance was run on the results of the five selected samples. A significant difference was found between the relative viscosities at the 0.1 percent level with both age and depth. Duncan's Multiple Range Test showed a significant difference between each pair of adjacent layers at the 1.0 percent level.

The graphs of viscosity versus depth of each individual sample are shown in the Appendix, Figures 15-28. Except for samples 3 and 13 an appreciable increase is seen in viscosity in layer A over layer B. Duplicate recoveries were performed on these samples, and the results were within 14 percent for sample 3 and two percent for sample 13 of the original tests. The most apparent reason for the viscosity of layer A to be less than layer B is the possibility of a fog seal or emulsion slurry seal being used to rejuvenate the pavement. This is quite possible for sample 13, as it is over 12 years old. However, there is no record of this having been done in either case.

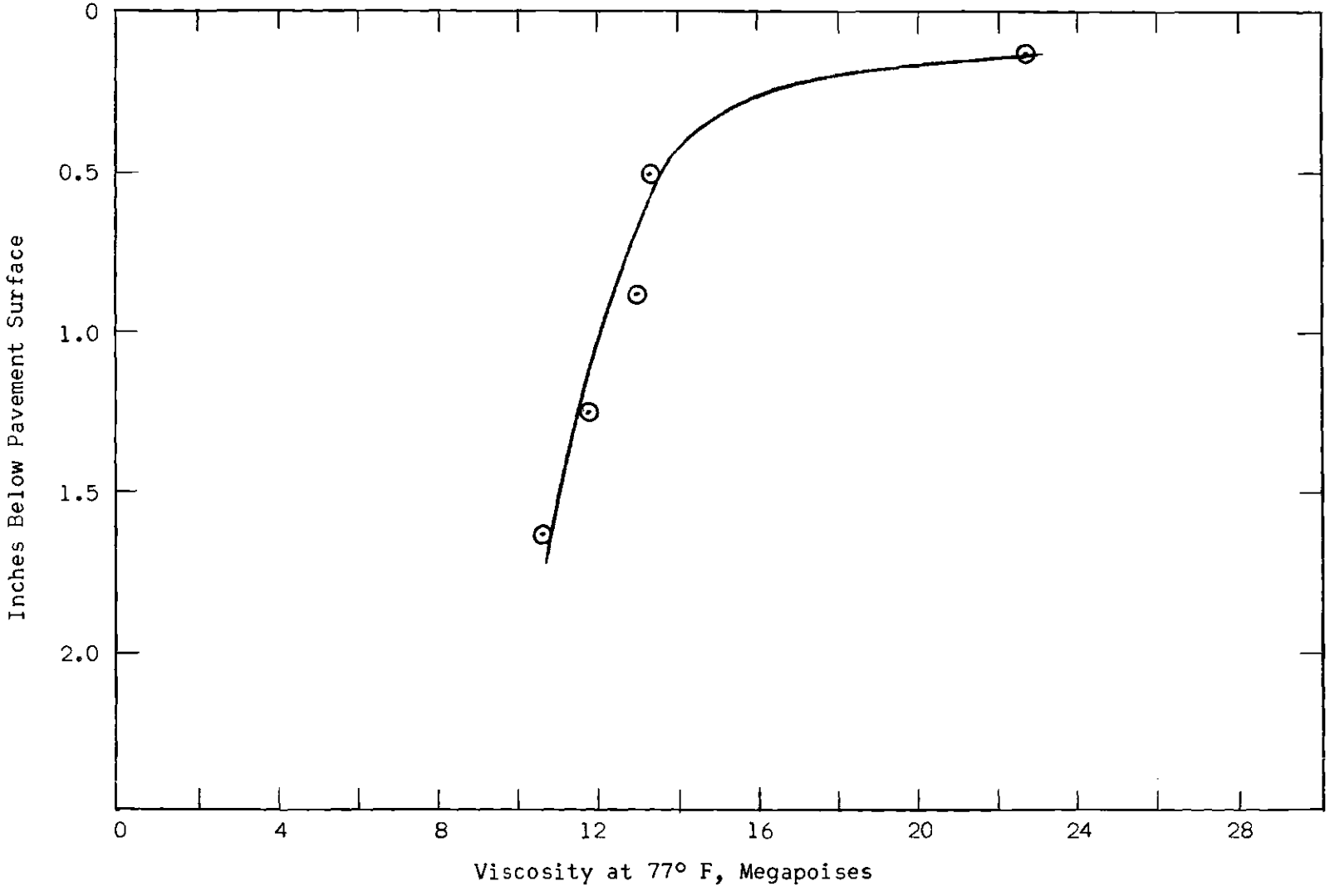

Figure 9. Average Viscosity of Samples 1, 2, 6, 11 and 13 Versus Depth.

Viscosity Versus Age

Figure 10 shows a composite graph of the relative viscosity as a function of age for each layer. In general, it shows that relative viscosity increases with age, except for layer E. The rate of change is more rapid in the top layer and decreases with increasing depths. Layer D is of interest in that there is no appreciable change in viscosity with time except for an initial increase. The initial increase probably occurred before or during placing and the later oxidation did not penetrate to this depth in the pavement. It would seem likely that with time the upper layers would disintegrate enough to affect layer D, and it, too, would increase in viscosity. But the figure indicates that this would be sometime beyond the expected life of 20 years. By that time layers A and B would be well disintegrated. Thus, at layer D relative viscosity appears to be independent of age. (See Figures 29-33.)

Relative Viscosity Versus Original Viscosity

The question logically arises as to what Figure 10 means with respect to original viscosity. It will be remembered that all samples 47 months or older are AC-8; those less than 47 months are AC-6. There is a difference between the original average viscosities of the two series. In this case, the difference is 1.08 megapoises. This suggests the possibility that the change in relative viscosity with age could be a function of original viscosity instead.

To evaluate this possibility a composite graph of relative viscosity versus original viscosity for each layer is shown in Figure 11. It shows that for layers A and B, and to some extent C, a high initial viscosity will result in less change than a low initial viscosity. Again, layer D

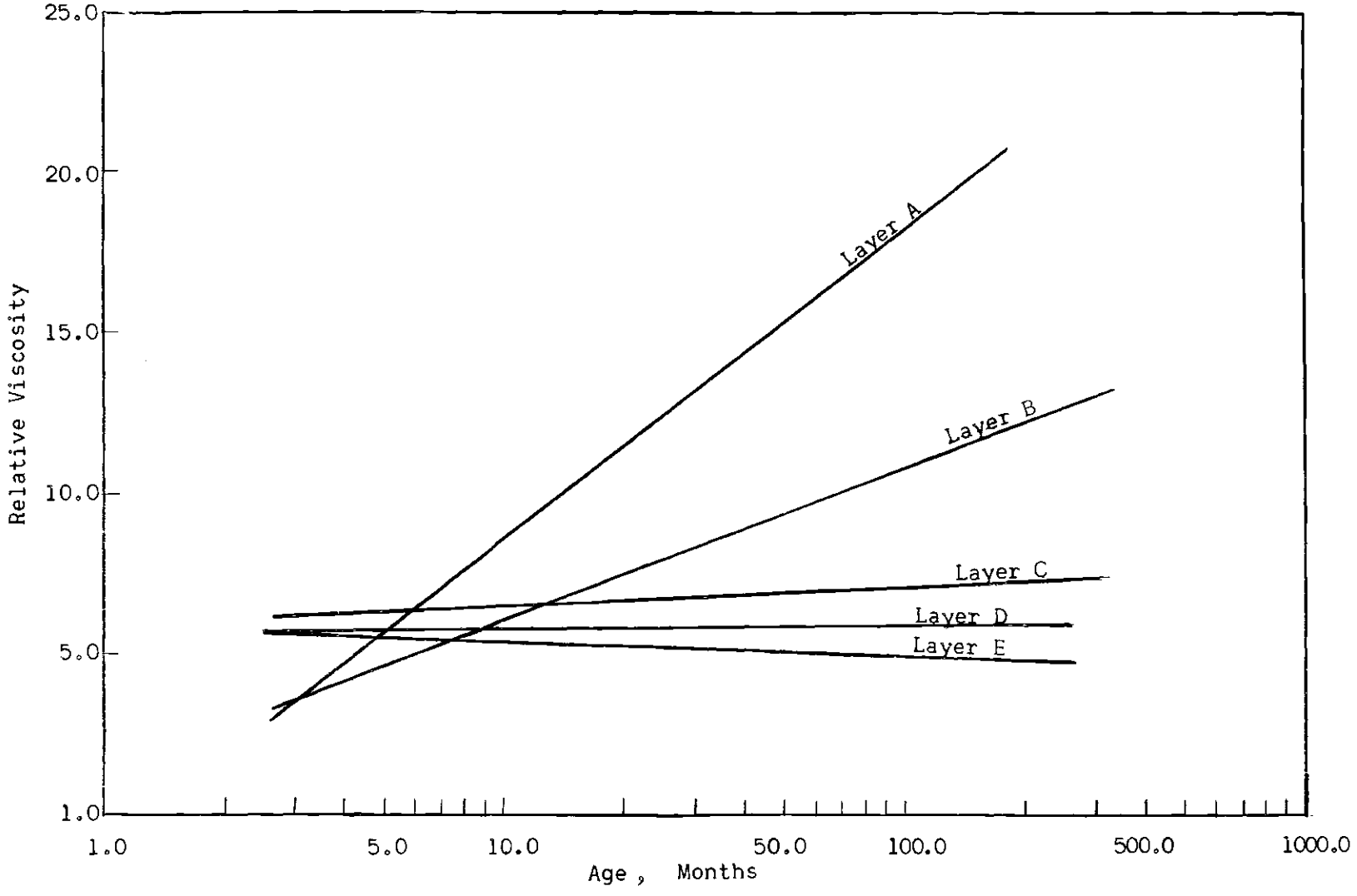

Figure 10. Relationship Between Relative Viscosity and Age.

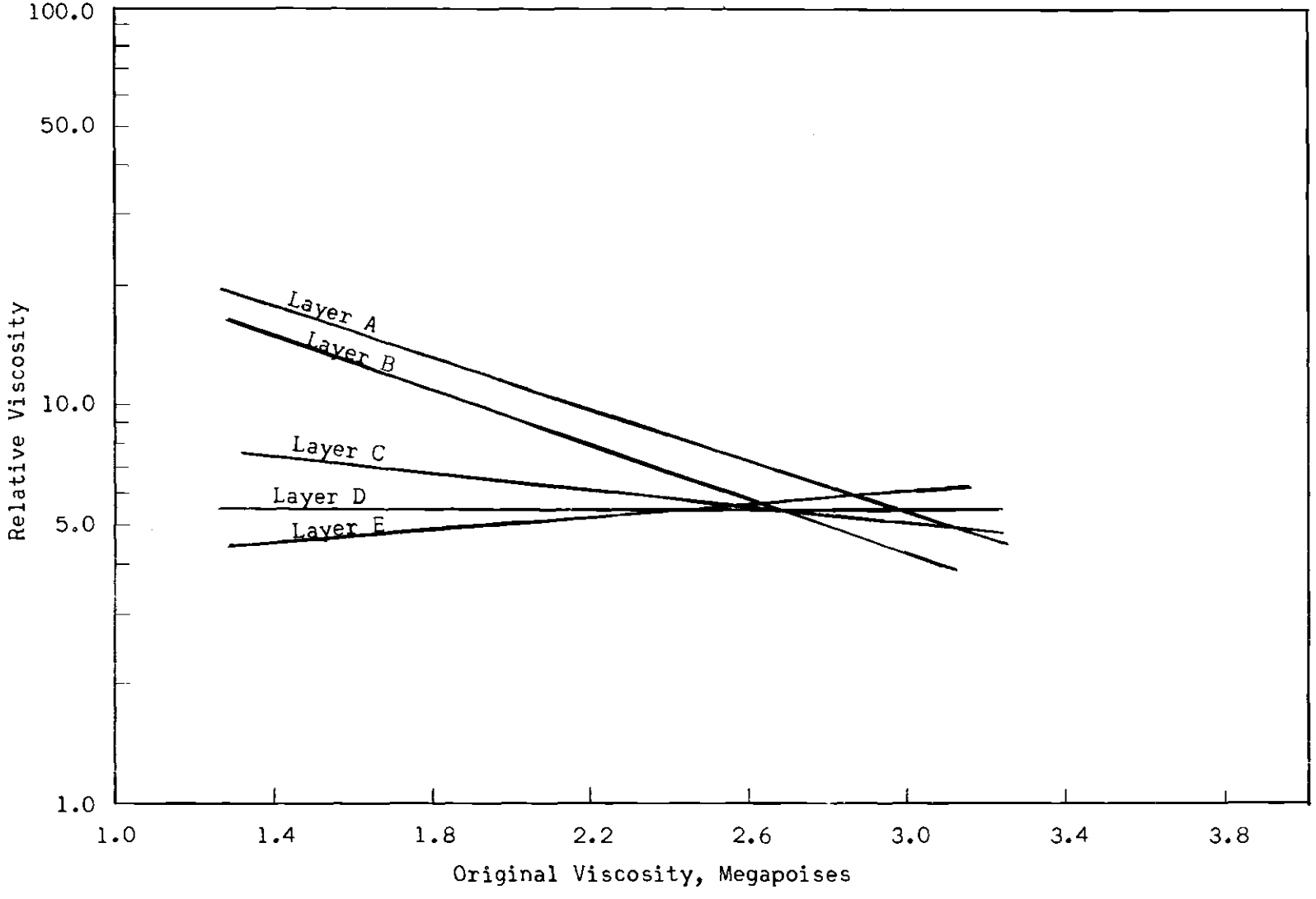

Figure 11. Relationship Between Relative Viscosity and Original Viscosity.

is of special interest, showing that relative viscosity, essentially, is independent of original viscosity at this depth. Regardless of the grade and original viscosity, the relative change at this depth will be the same. (See Figures 34 - 38.)

Returning to Figure 10, one would conclude from the previous paragraph that for layer D at least, the relationship is true and independent of original viscosity. From the statistical analysis of relative viscosity versus age, there was no significant difference at the 5.0 percent level between layers C, D, and E. Thus the relative viscosity versus original viscosity relationships for layers C and E in Figure 11 may also be considered true.

For layers A and B no conclusive statement may be made as a result of Figures 10 and 11. Relative viscosity is influenced by both age and original viscosity, but the relative importance of each may not be determined. It can be stated, however, that viscosity does increase with age. But how this increase is influenced by original viscosity was not determined.

Spectrophotometer Study

The results of the spectrophotometer study are shown in Table 5. Sample A represents the top quarter inch; sample B represents the next underlying layer from 0.375 to 0.625 inch below the surface. The transmittance at 2.91, 5.88, and 9.71 microns are shown representing the wavelengths at which the changes in asphalt structure are most evident. The hydroxyl band is 2.91 microns, the carbonyl is 5.88 and the carbon-oxygen is 9.71. A difference in the transmittance of one of these wavelengths

Table 5. Spectrophotometer Results

Sample No.	Age (mo)	Thickness (microns)	2.91 Micron	5.88 Micron	9.71 Micron
1 A	4	72	67	55	49
1 B	4	73	69	60	51
6 A	10	77	38	32	13
6 B	10	79	33	34	10
8 A	24	76	64	50	30
8 B	24	78	68	60	32
9 A	47	76	55	35	24
9 B	47	78	55	52	32
10 A	70	78	61	32	27
10 B	70	76	62	42	30
12 A	126	79	49	27	19
12 B	126	79	44	31	17

indicates a change in the molecular structure of the atoms observed at that wavelength. But this does not necessarily indicate the cause of the change. It is generally believed that oxidation is the cause; but it is not known whether this occurs during mixing, placement, or service life. The largest differences appear at 5.88 microns wavelength.

Figures 12, 13, and 14 give the results in better form. Since the data indicate a linear relationship, a regression line has been computed for each set of data.

Figure 12 shows the transmittance at 2.91 microns. The regression lines for layers A and B are almost parallel, with only a slight difference in the rate of decrease in transmittance with increasing age. An analysis of variance was run on the data, indicating a significant difference in transmittance with age at the 0.1 percent level. There is a significant difference in transmittance with depth at the 5.0 percent level.

Complete analysis of this variation is beyond the scope of this research. However, the data do indicate that the 2.91 micron wavelength may be used to determine aging but not to accurately determine difference in aging with depth.

In Figure 13, regression lines are shown for transmittance through the A and B layers at the 5.88 micron wavelength. Both indicate hardening with time as indicated by the decrease in transmittance with increasing age. The analysis of variance showed a significant difference in transmittance with time at the 0.1 percent level and with depth at the 1.0 percent level. Thus, the effect of depth is more apparent at the 5.88 than at the 2.91 micron wavelength.

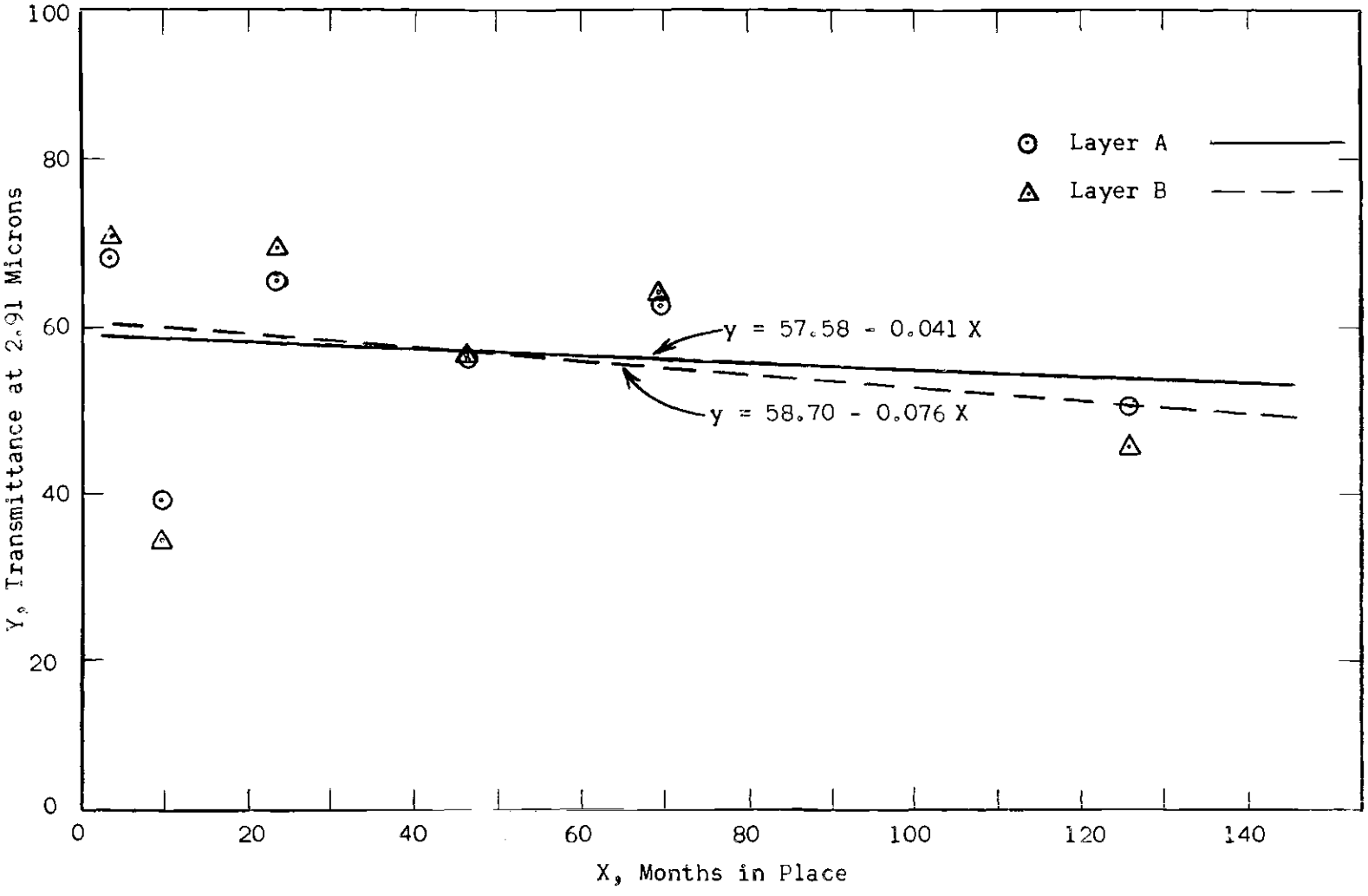

Figure 12. Relationship Between Infrared Transmittance at 2.91 Microns and Age.

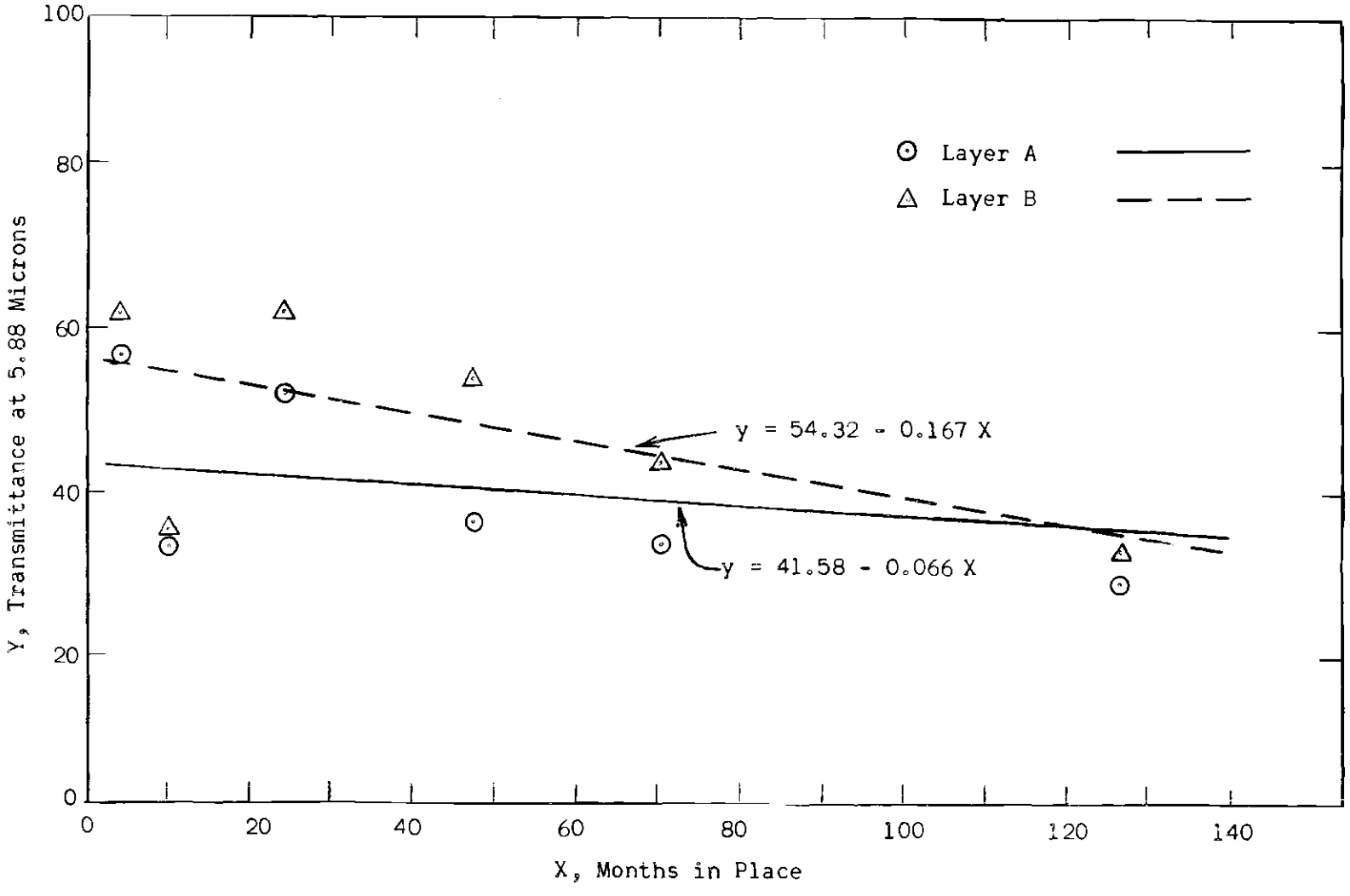

Figure 13. Relationship Between Infrared Transmittance at 5.88 Microns and Age.

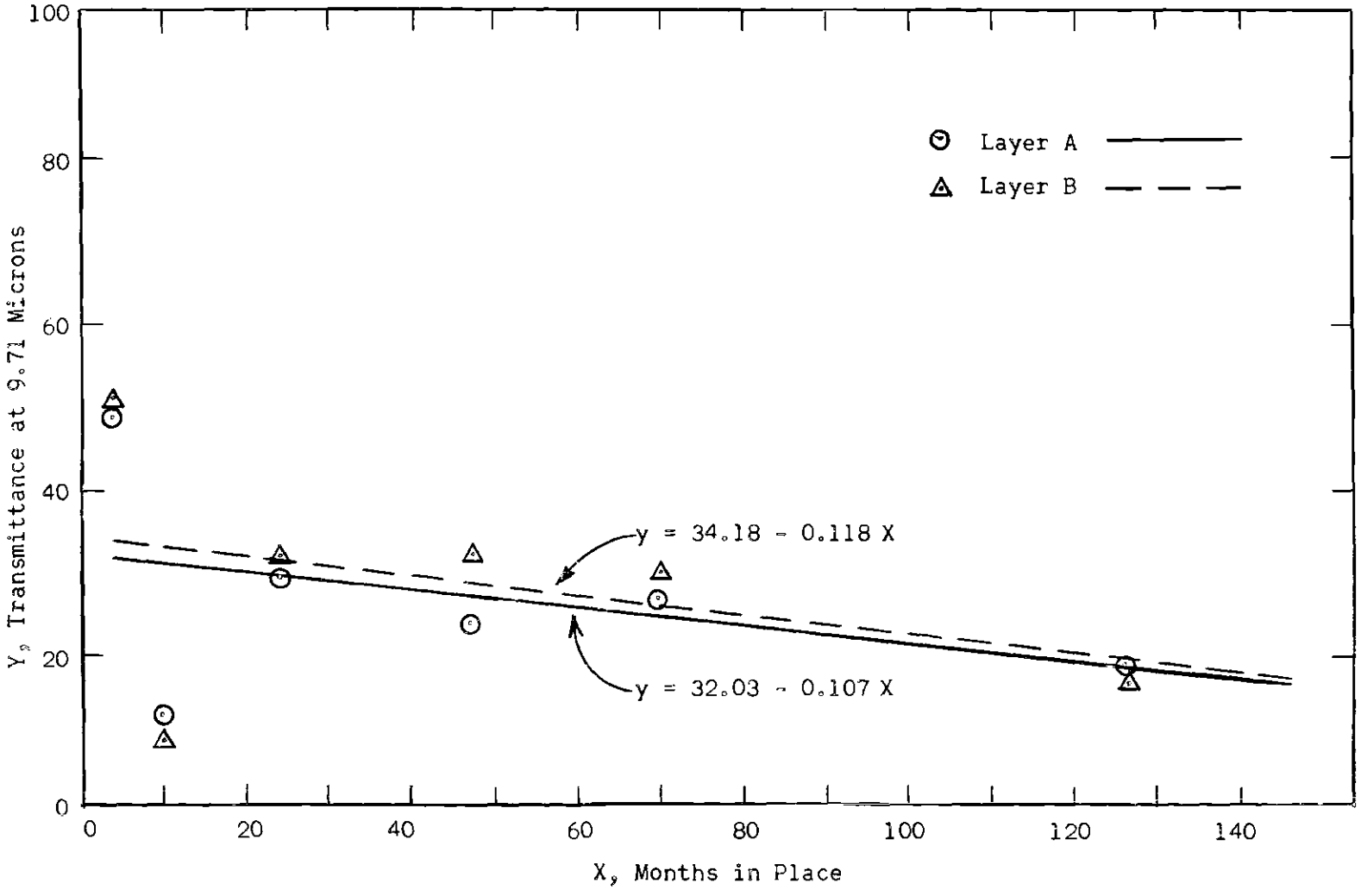

Figure 14. Relationship Between Infrared Transmittance at 9.71 Microns and Age.

The greater slope of the B regression line indicates that the B layer is hardening at a faster rate than the A layer. But the transmittance through the A layer is less than that through the B layer up to about 120 months, indicating that hardening has already occurred in the surface layer. Since the difference at young ages is large and the rate of change in transmittance in A is small, the major change probably occurred before or during placement. This is easily explained as there are more exposed surfaces before and during placement.

These data indicate that the 5.88 micron wavelength is a good indicator of changes in asphalt with age.

Figure 14 shows the transmittance of the 9.71 micron wavelength as a function of pavement age. There is a significant difference in transmittance with age at the 0.1 percent level but no significant difference with depth at the 5.0 percent level. Therefore, there has been little change in the carbon-oxygen bond due to depth. It is apparent that this wavelength will give only limited indication of oxidation with depth.

These results, Figures 12, 13, and 14, show a significant difference at the 0.1 percent level in transmittance with age for each wavelength. While there is a significant difference in transmittance with depth at the 5.0 percent level for 2.91 micron wavelength, the difference at 5.88 is more significant. This is in agreement with previous research showing changes in the carbonyl band are the best indicators of oxidation.

Thus, any of the three wavelengths may be used to show hardening with time but the 5.88 micron wavelength is best to show hardening with depth.

CHAPTER VI

CONCLUSIONS AND RECOMMENDATIONS

Conclusions

The results of this study indicate the following conclusions for the asphalt pavements studied:

1. There is about 50 percent increase in the viscosity of asphalt extracted from the top quarter inch of a pavement over asphalt extracted from depths to one-half inch.

2. Within the top quarter inch layer there is a greater viscosity immediately under the surface than lower in the layer.

3. Viscosity in the upper one-half inch increases with age while little change with age occurs at greater depths.

4. At a depth of about one and one-half inches below the pavement surface, there is little change in viscosity with age except for an initial increase during or before placing.

5. At a depth of about one and one-half inches below the pavement surface, the relative viscosity is independent of original viscosity.

6. A spectrophotometer may be used to indicate hardening. The 5.88 micron wavelength gives the best measure of change with depth but the 2.91 and 9.71 micron wavelengths may be used to study increases in hardening with age.

Recommendations

On the basis of this research the following recommendations are made:

1. A study should be made of change in viscosity at various depths below the pavement surface with age using only one grade of asphalt cement.

2. A study should be made of change in viscosity at various distances from the centerline of a roadway with age.

3. The spectrophotometer should be more extensively and effectively utilized as an asphalt research instrument.

APPENDIX

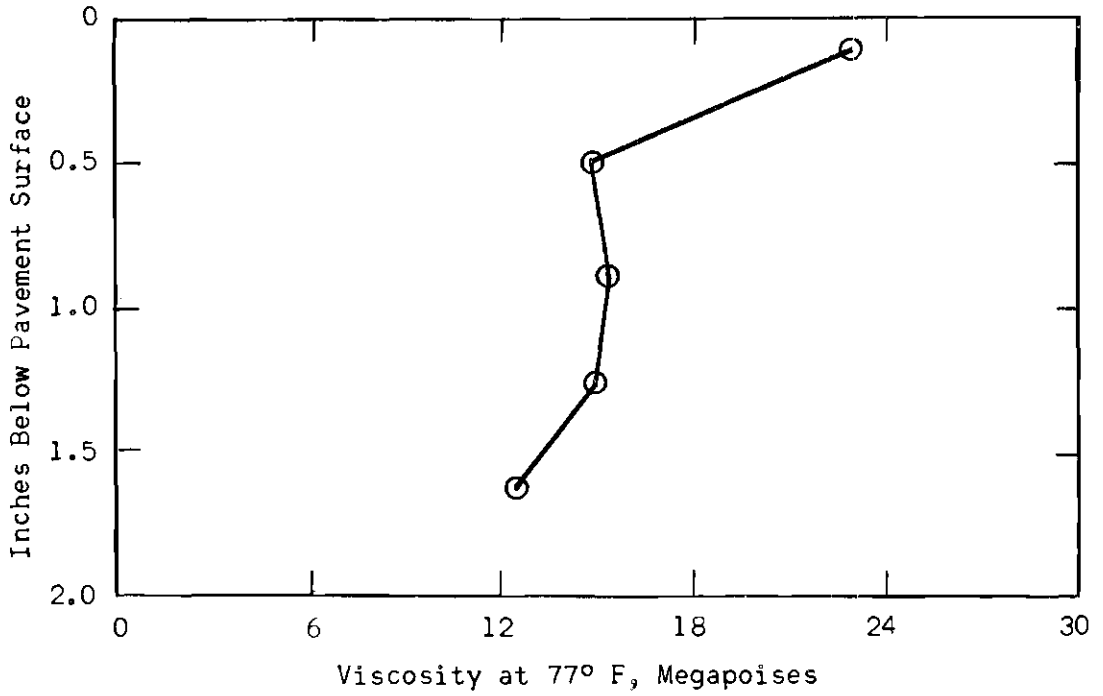

Figure 15. Viscosity of Sample 1 as a Function of Depth.

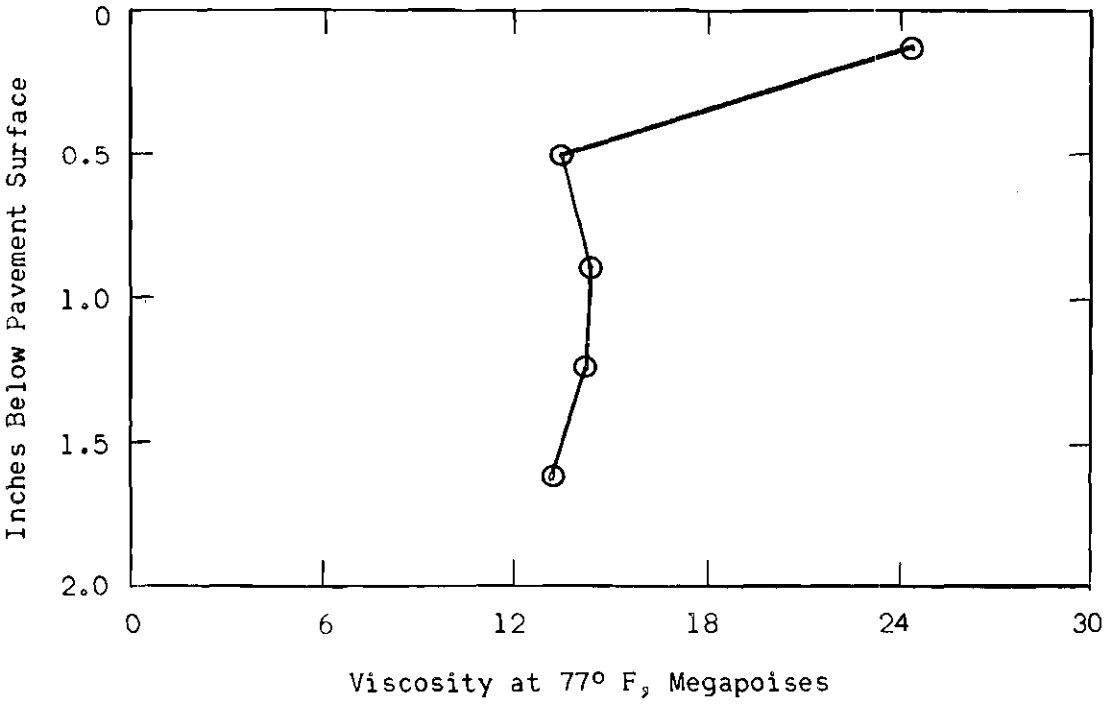

Figure 16. Viscosity of Sample 2 as a Function of Depth.

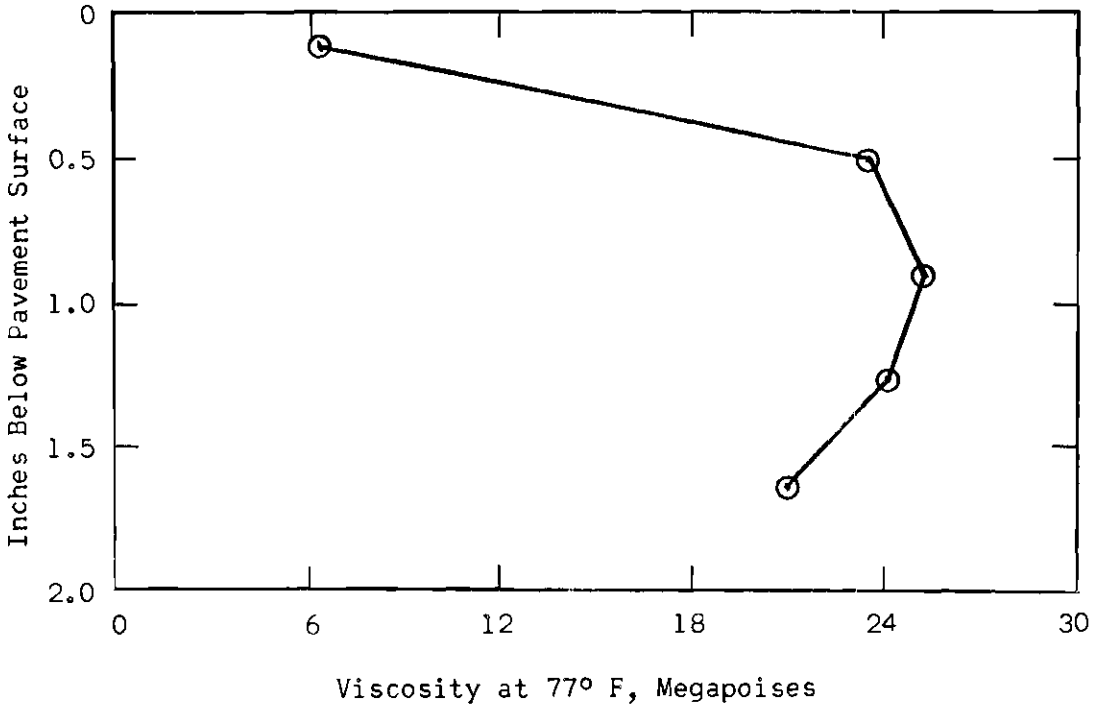

Figure 17. Viscosity of Sample 3 as a Function of Depth.

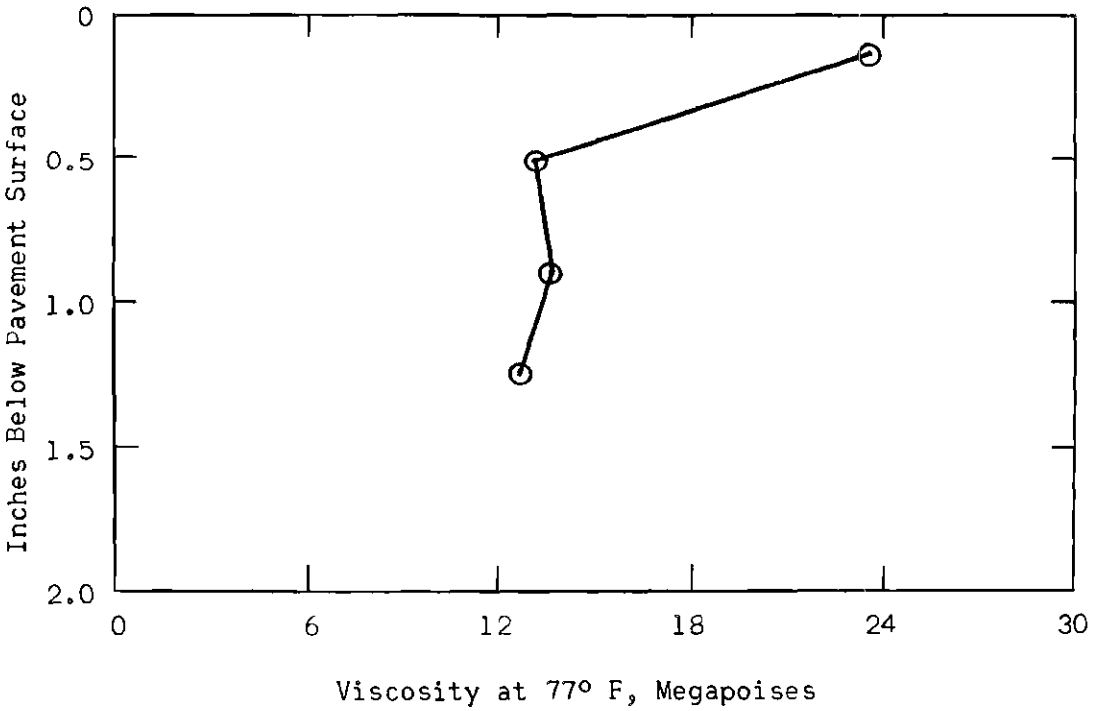

Figure 18. Viscosity of Sample 4 as a Function of Depth.

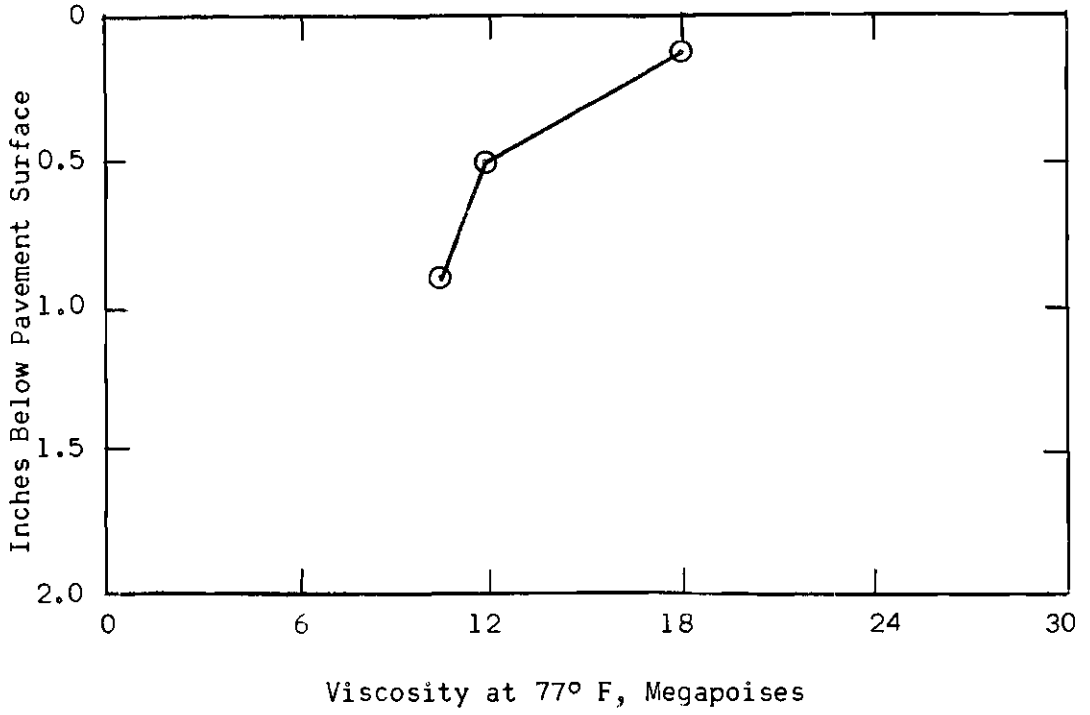

Figure 19. Viscosity of Sample 5 as a Function of Depth.

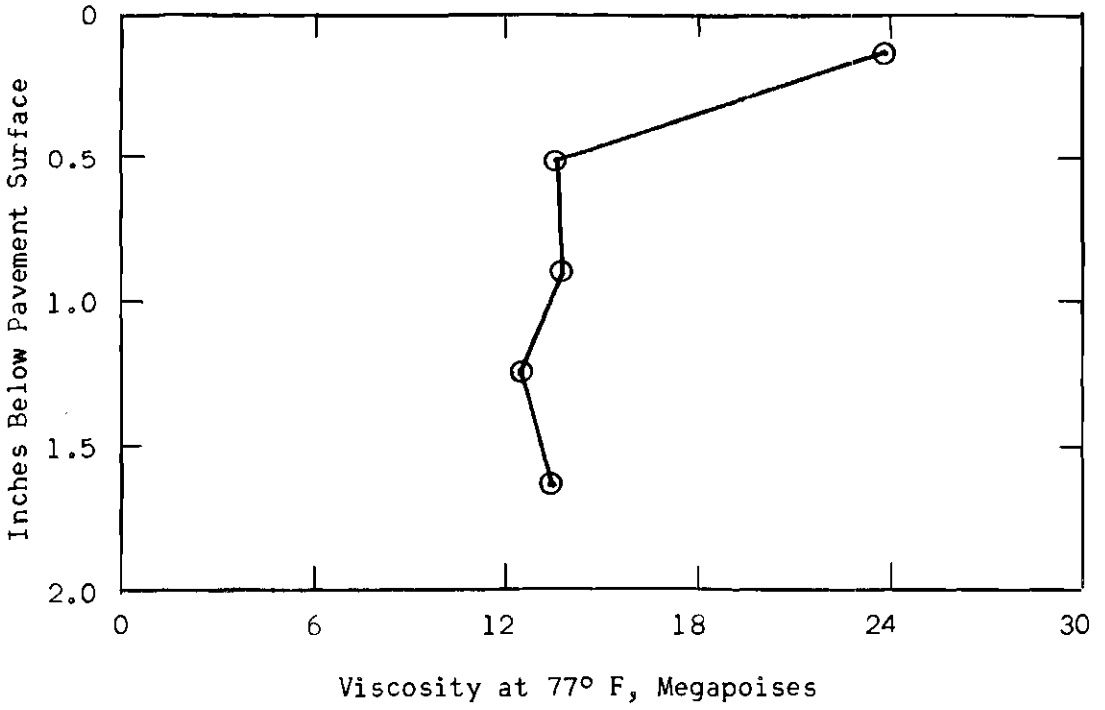

Figure 20. Viscosity of Sample 6 as a Function of Depth

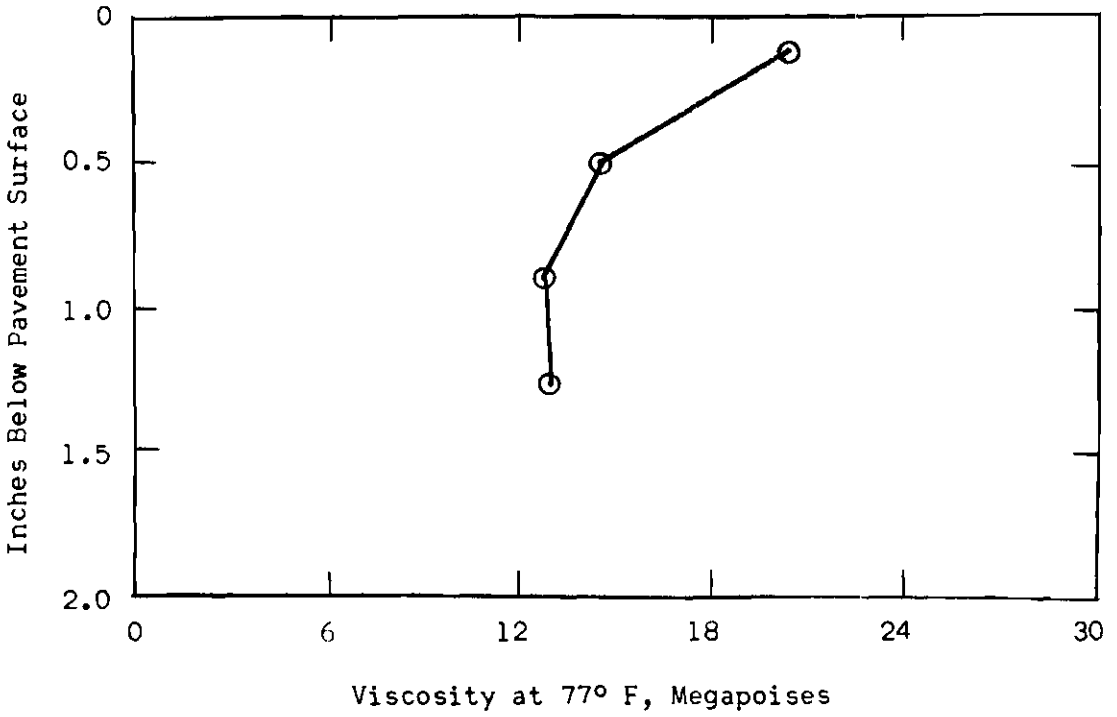

Figure 21. Viscosity of Sample 7 as a Function of Depth.

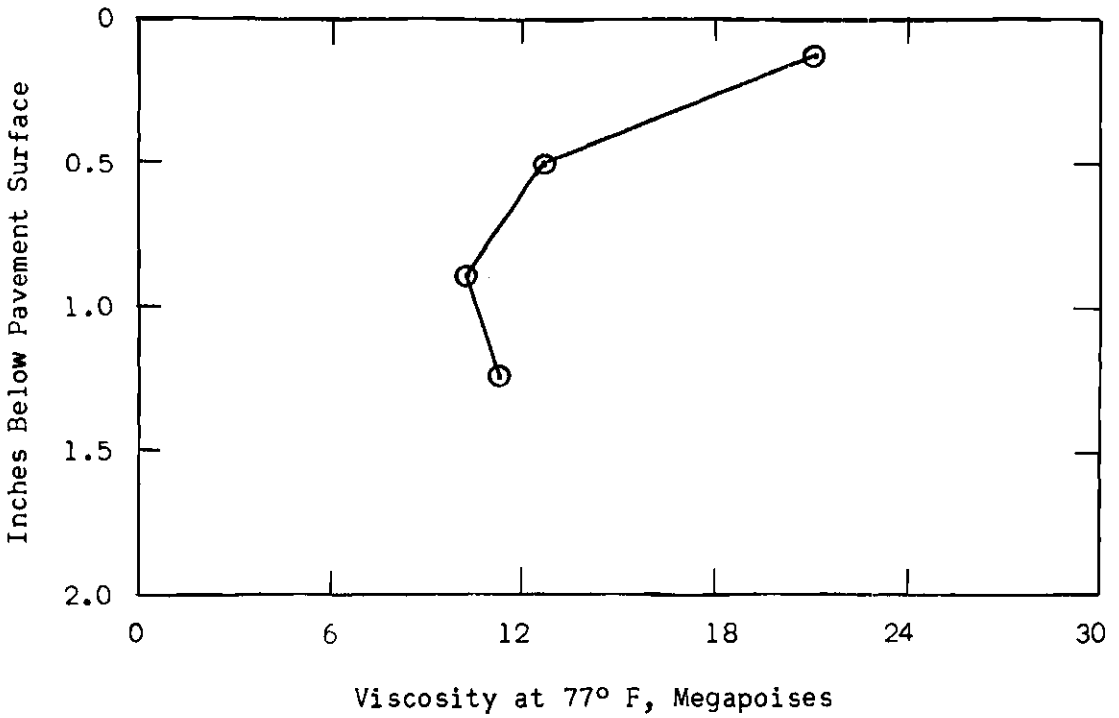

Figure 22. Viscosity of Sample 8 as a Function of Depth.

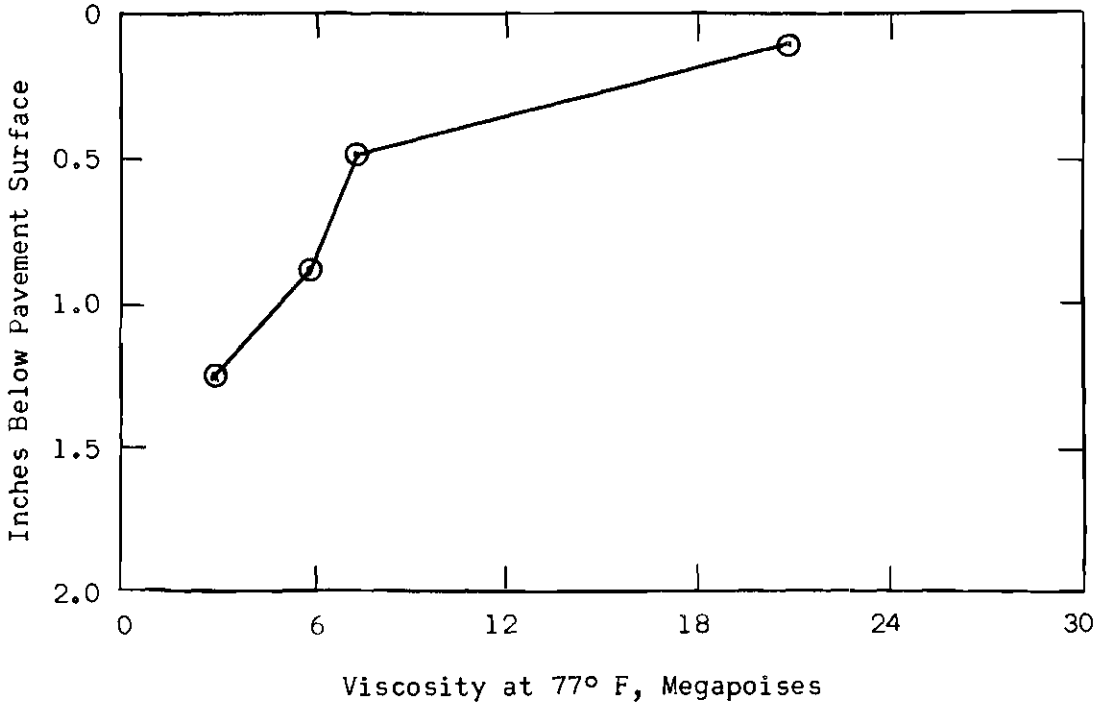

Figure 23. Viscosity of Sample 9 as a Function of Depth.

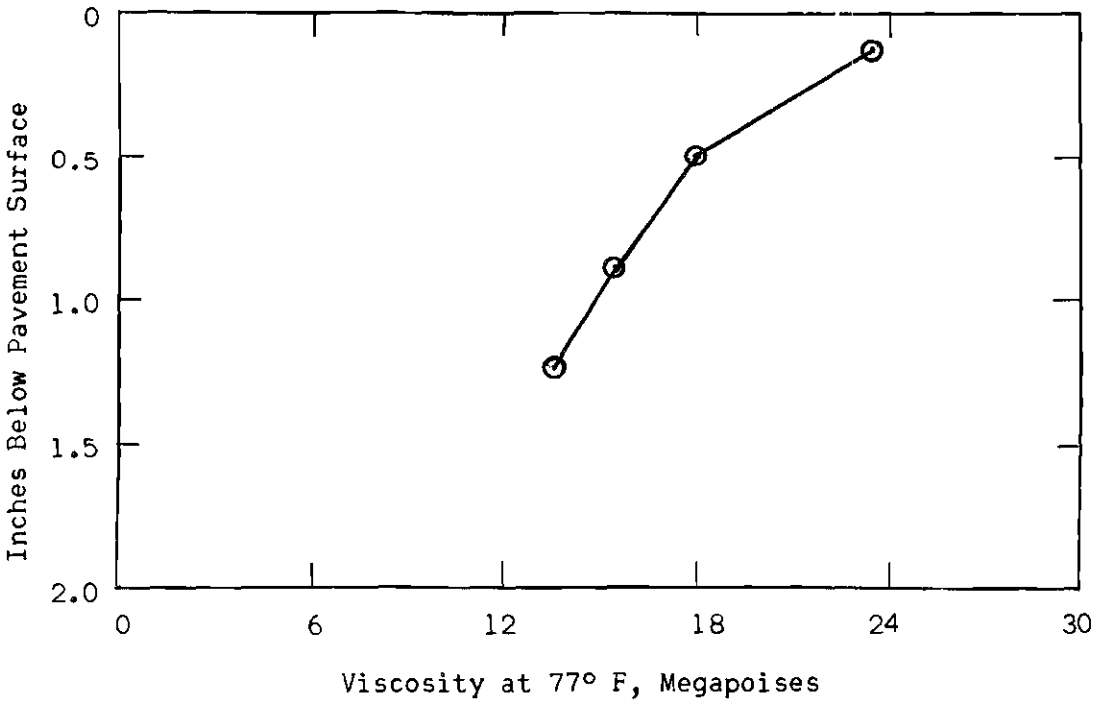

Figure 24. Viscosity of Sample 10 as a Function of Depth.

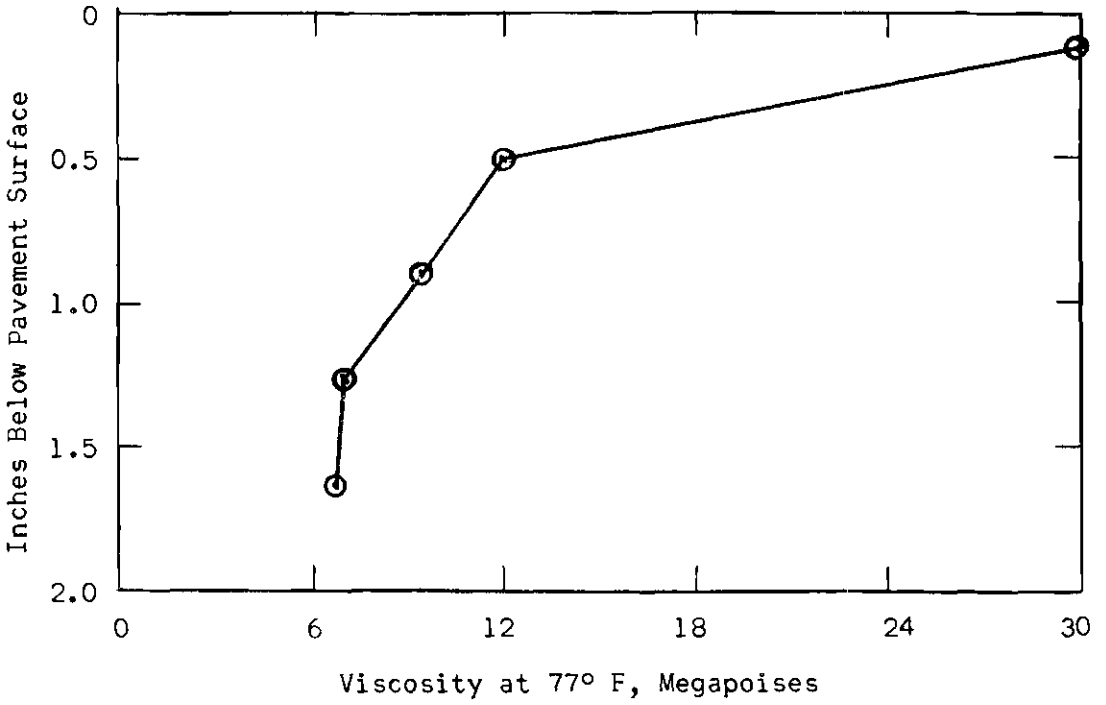

Figure 25. Viscosity of Sample 11 as a Function of Depth.

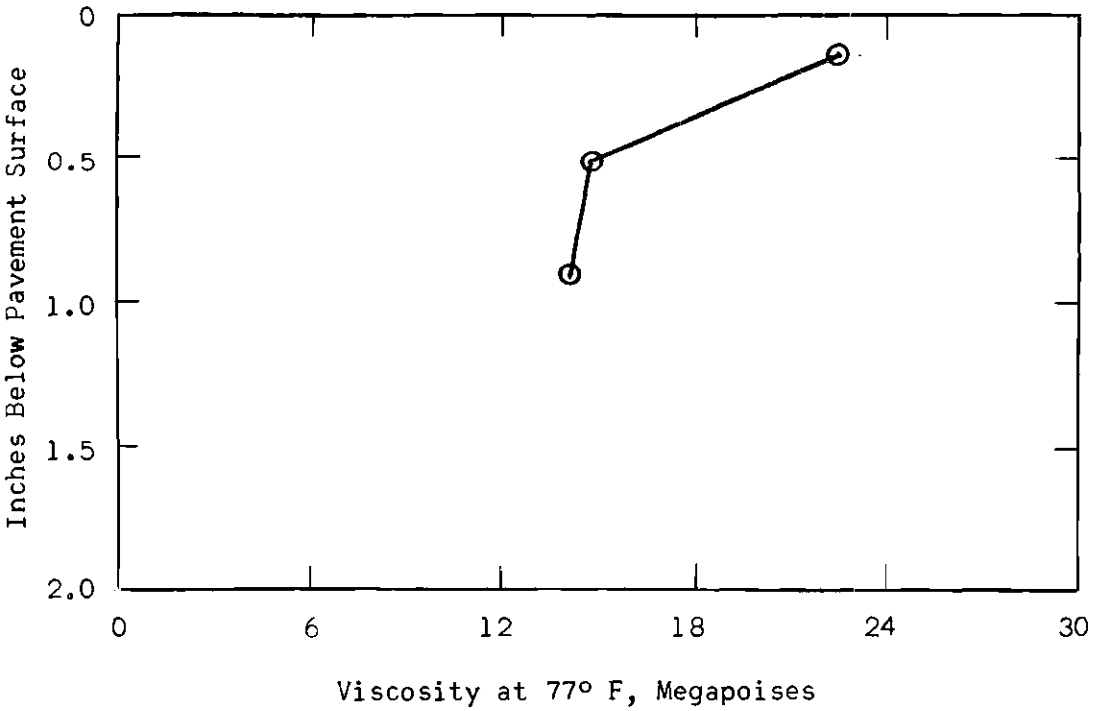

Figure 26. Viscosity of Sample 12 as a Function of Depth.

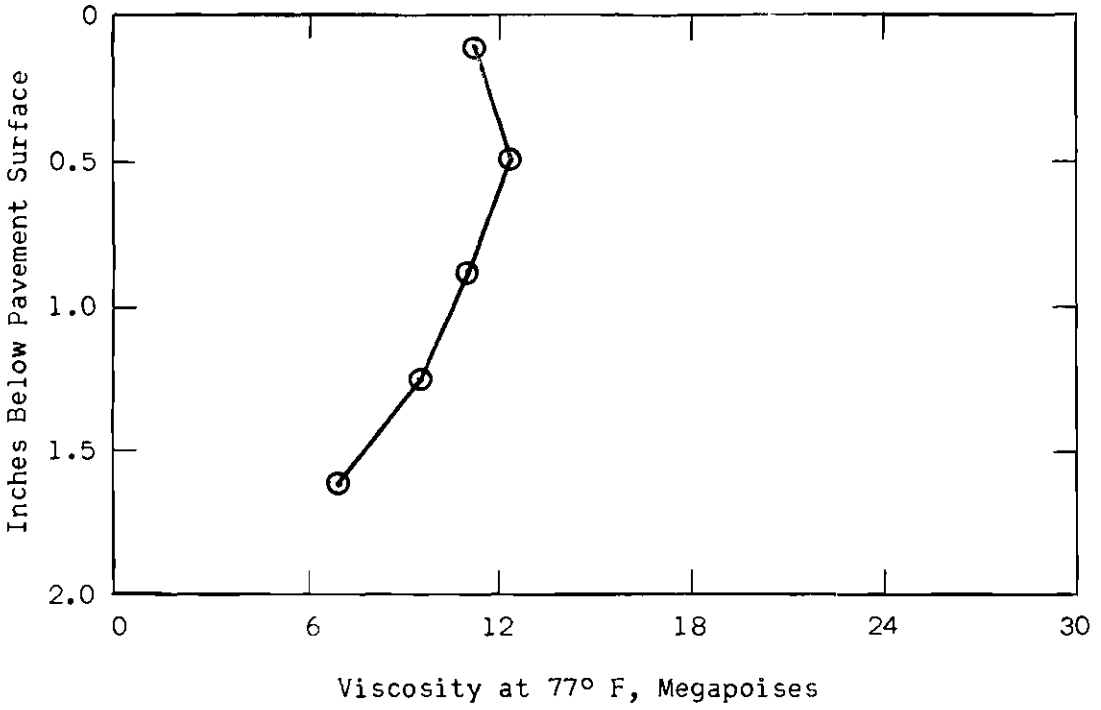

Figure 27. Viscosity of Sample 13 as a Function of Depth.

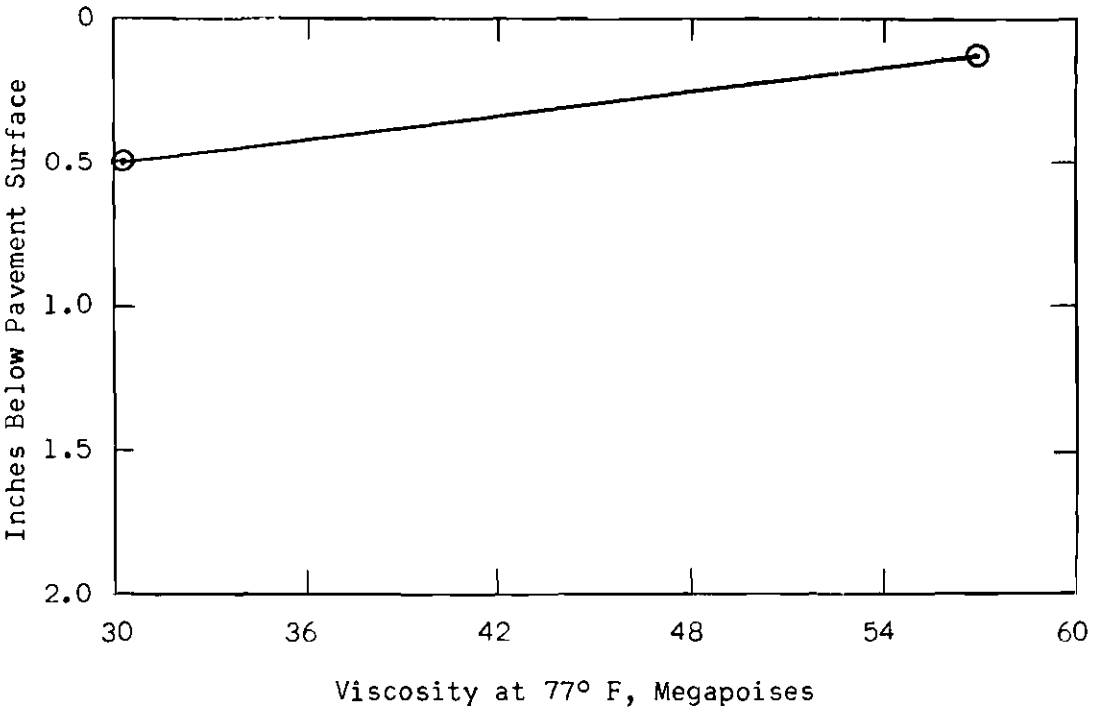

Figure 28. Viscosity of Sample 14 as a Function of Depth.

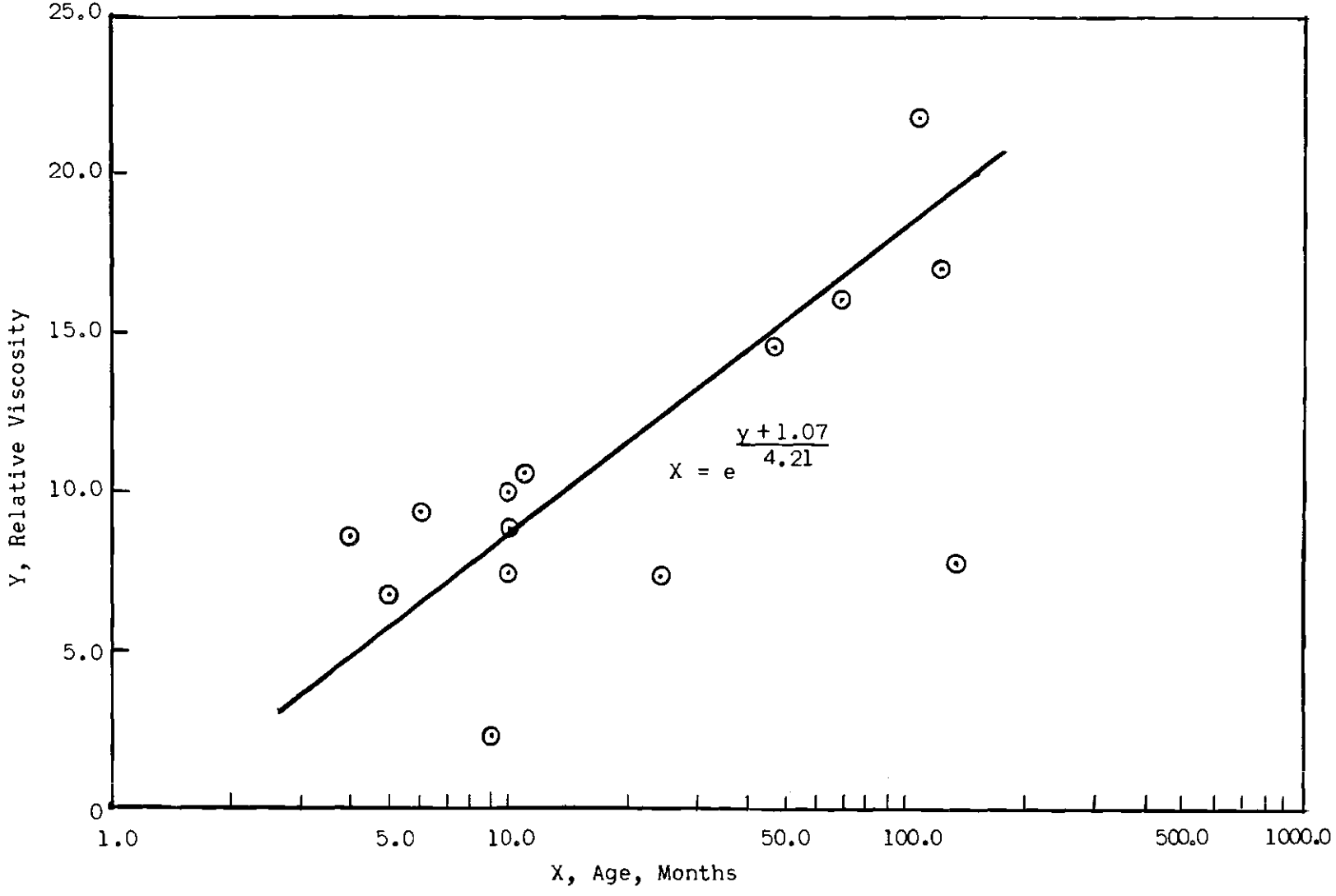

Figure 29. Relative Viscosity in Layer A Versus Age.

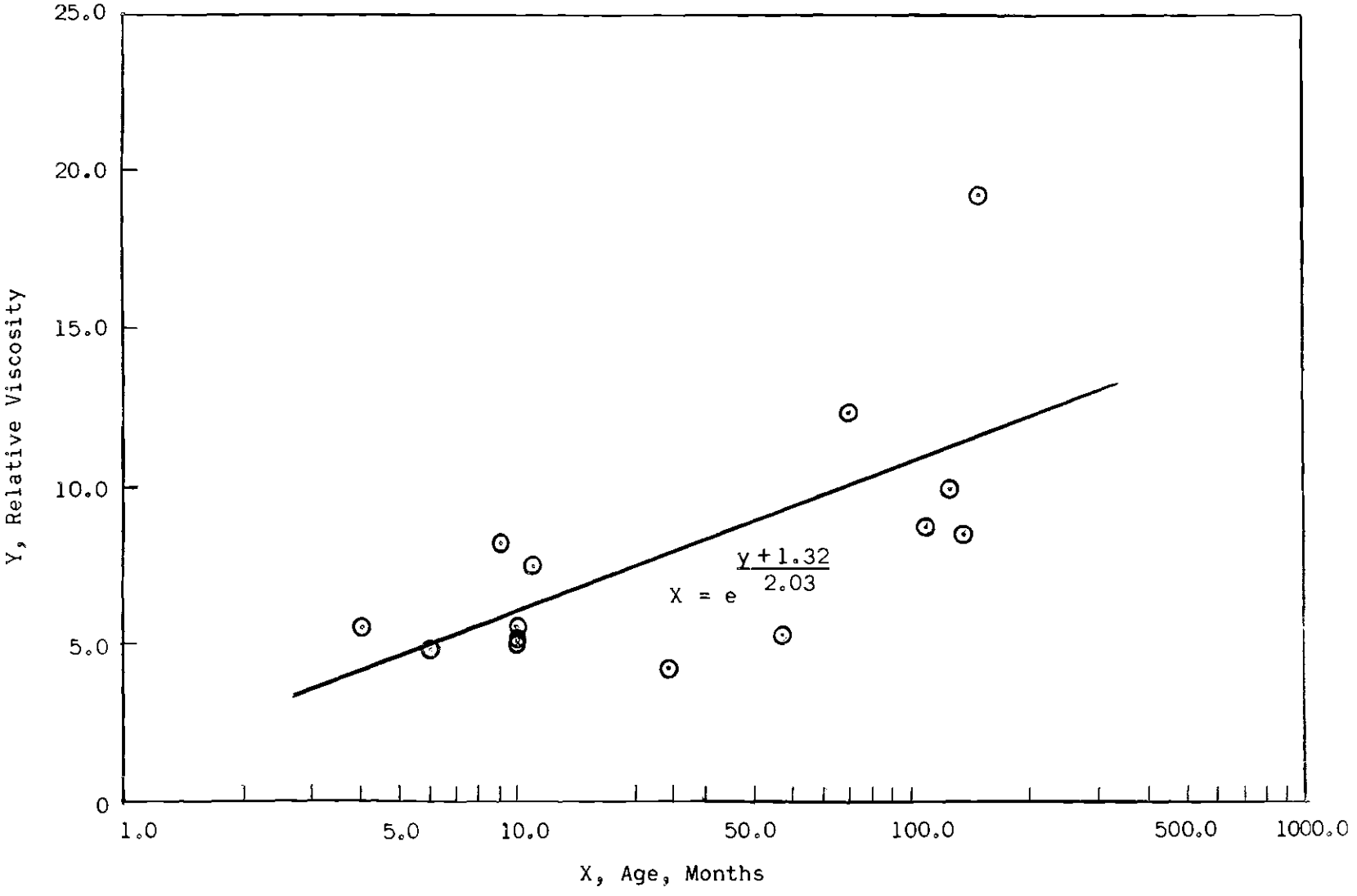

Figure 30. Relative Viscosity in Layer B Versus Age.

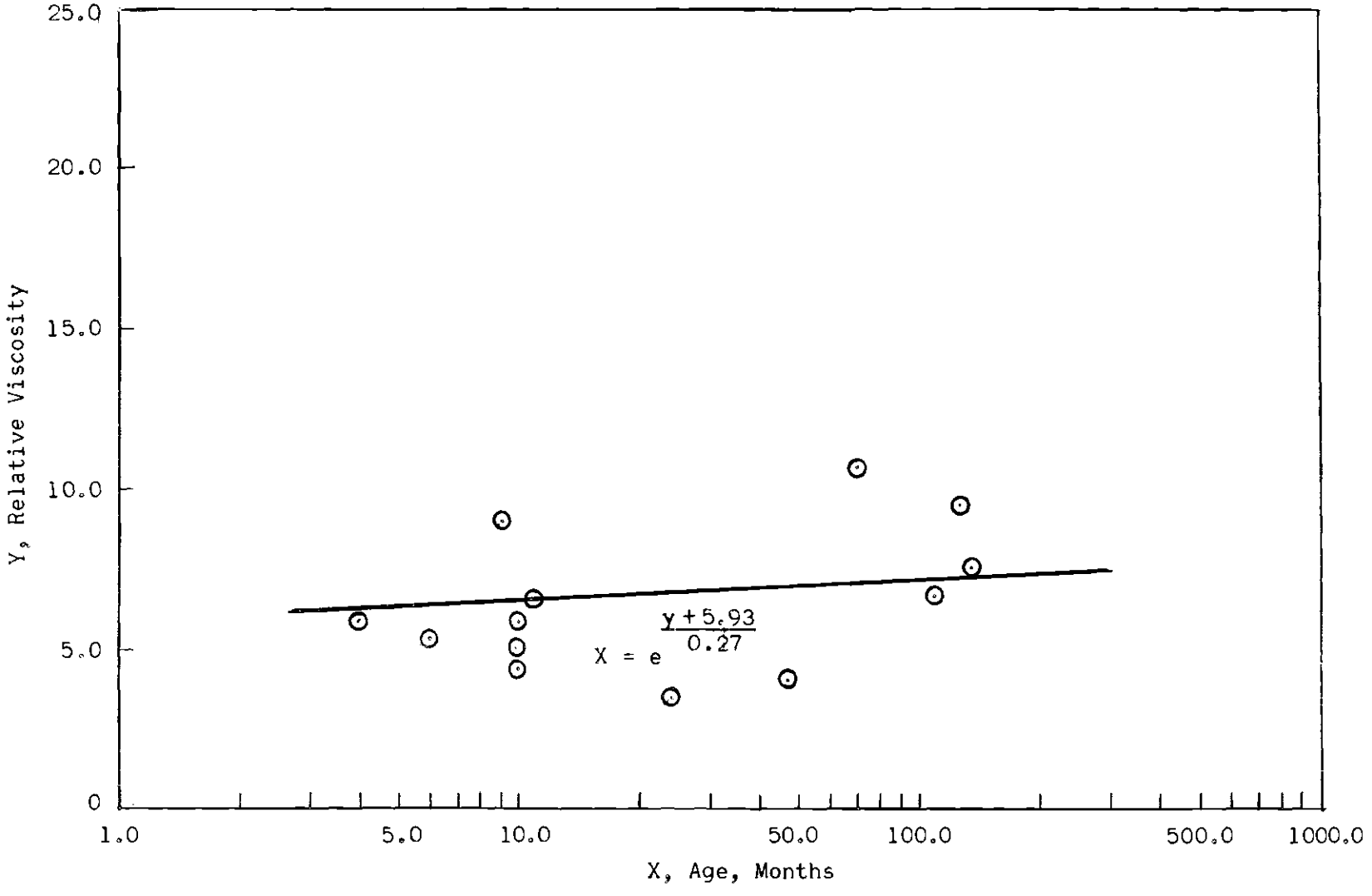

Figure 31. Relative Viscosity in Layer C Versus Age.

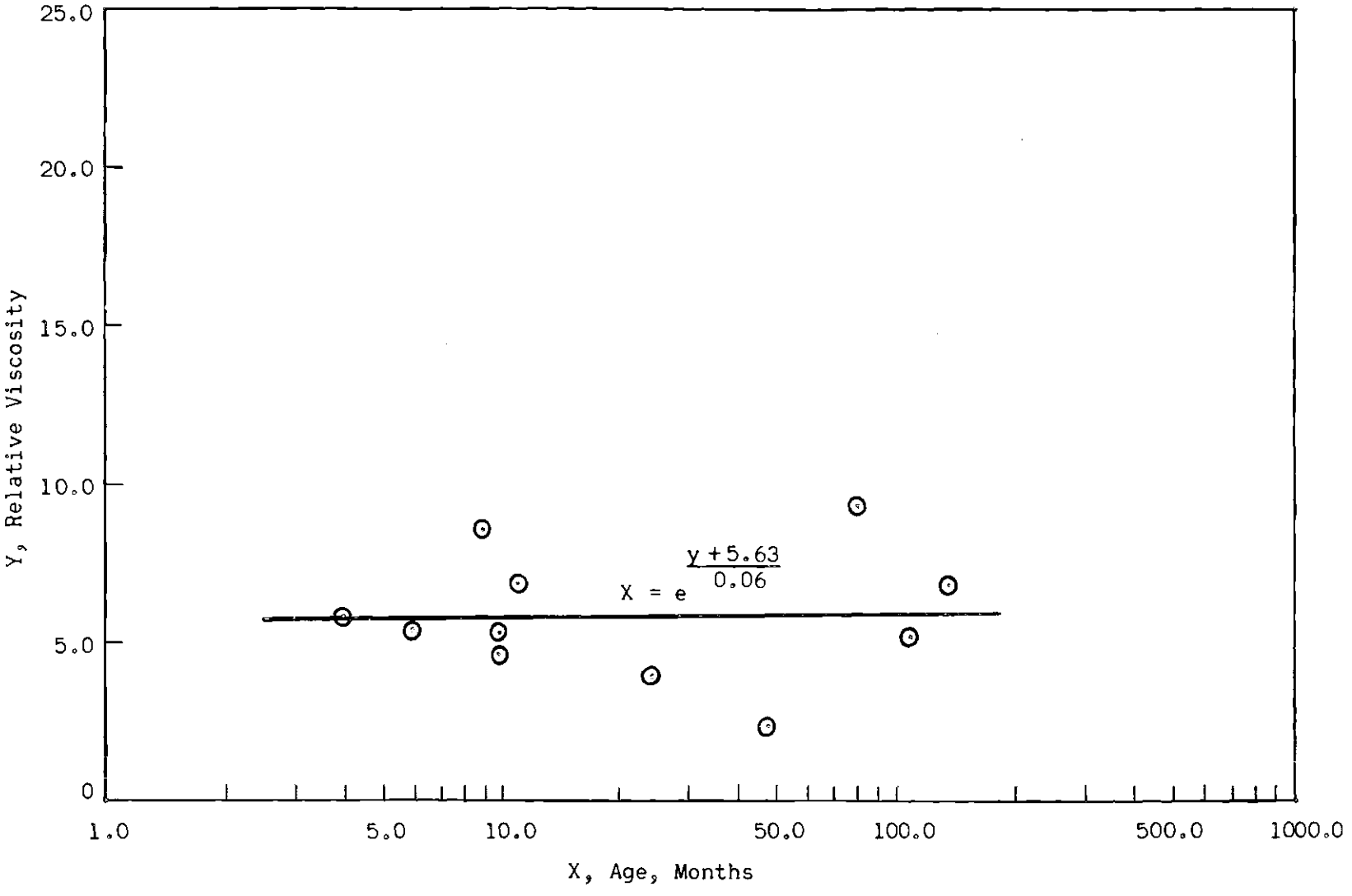

Figure 32. Relative Viscosity in Layer D Versus Age.

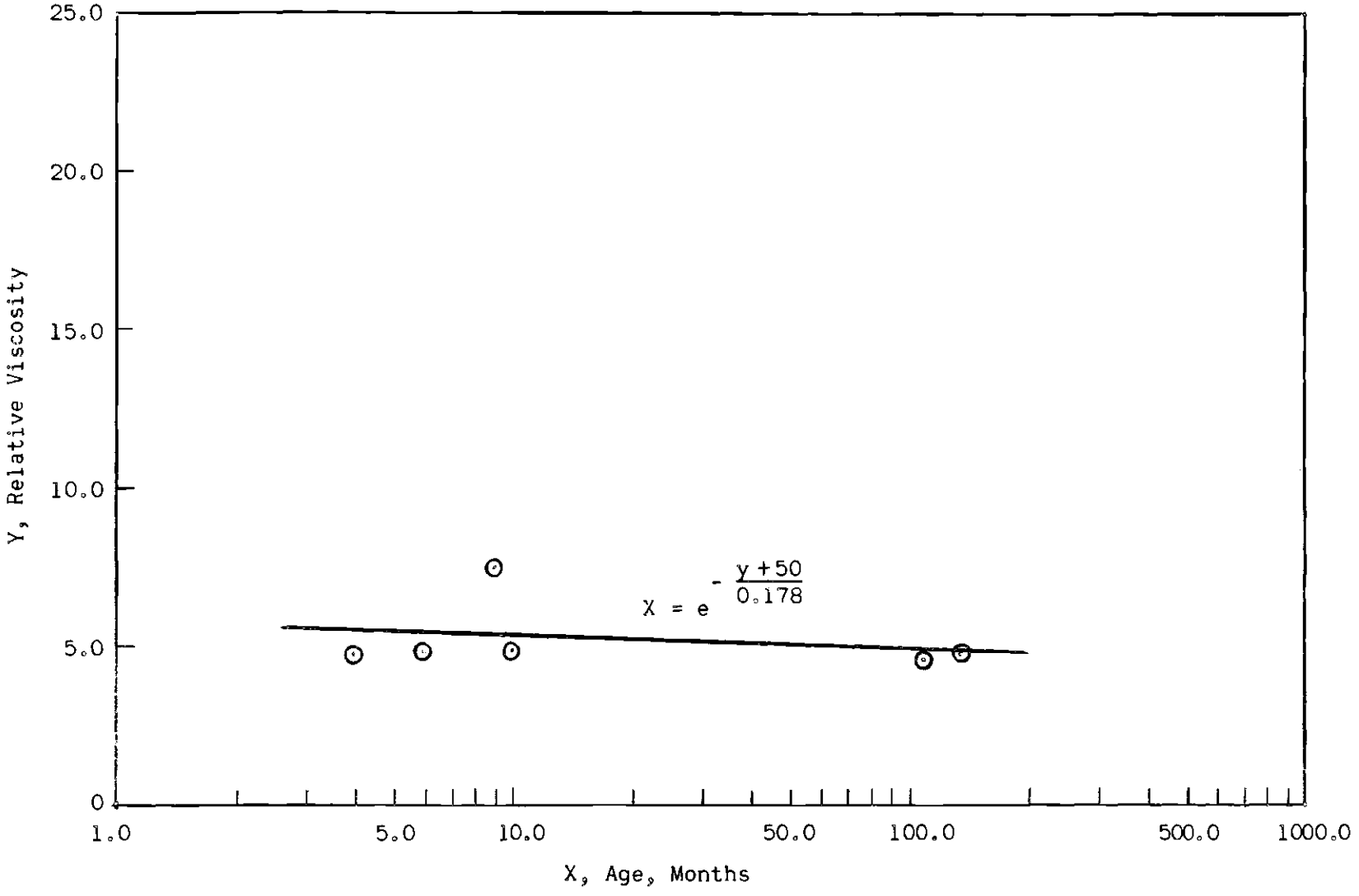

Figure 33. Relative Viscosity in Layer E Versus Age.

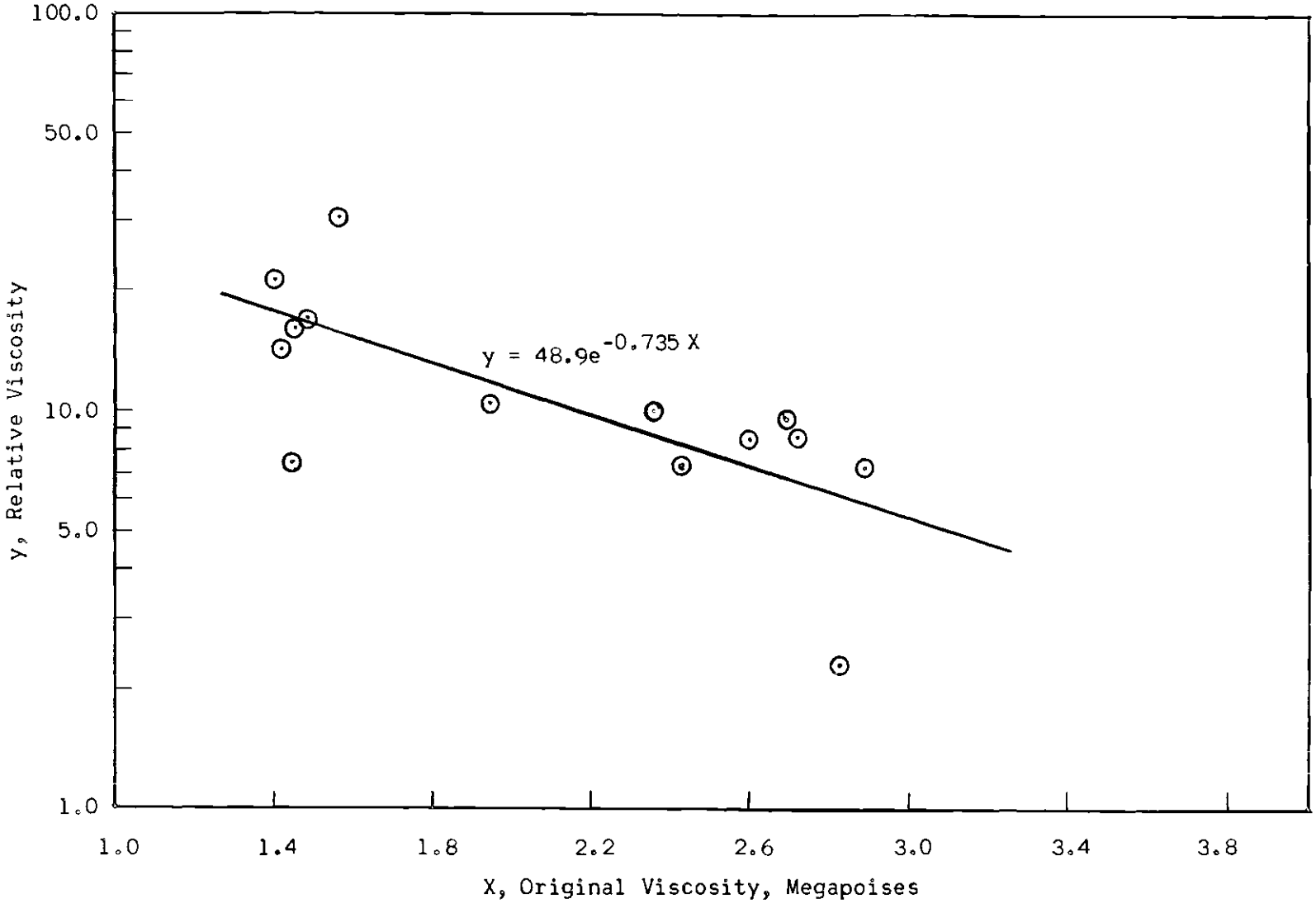

Figure 34. Original Viscosity versus Relative Viscosity for Layer A.

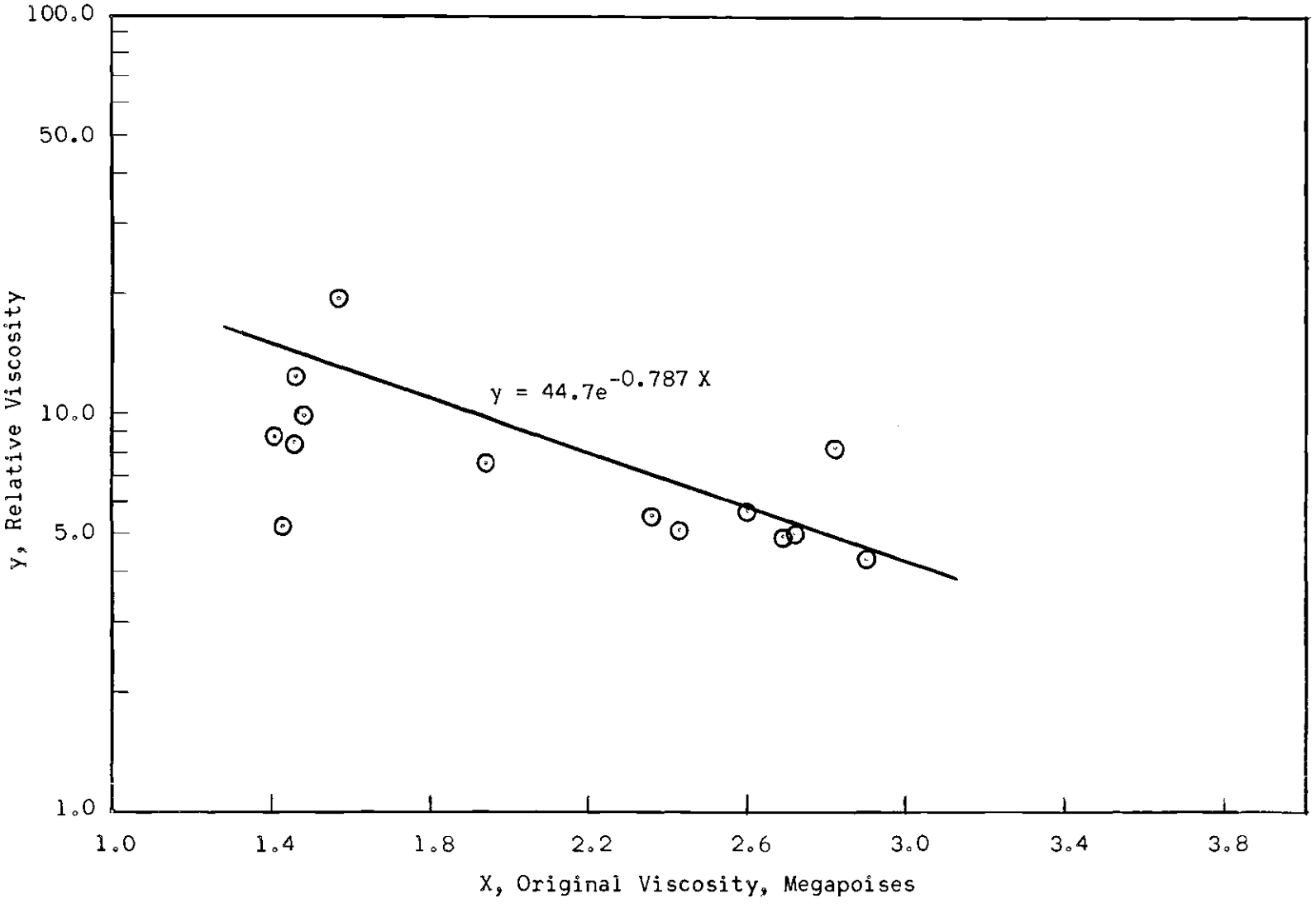

Figure 35. Original Viscosity versus Relative Viscosity for Layer B.

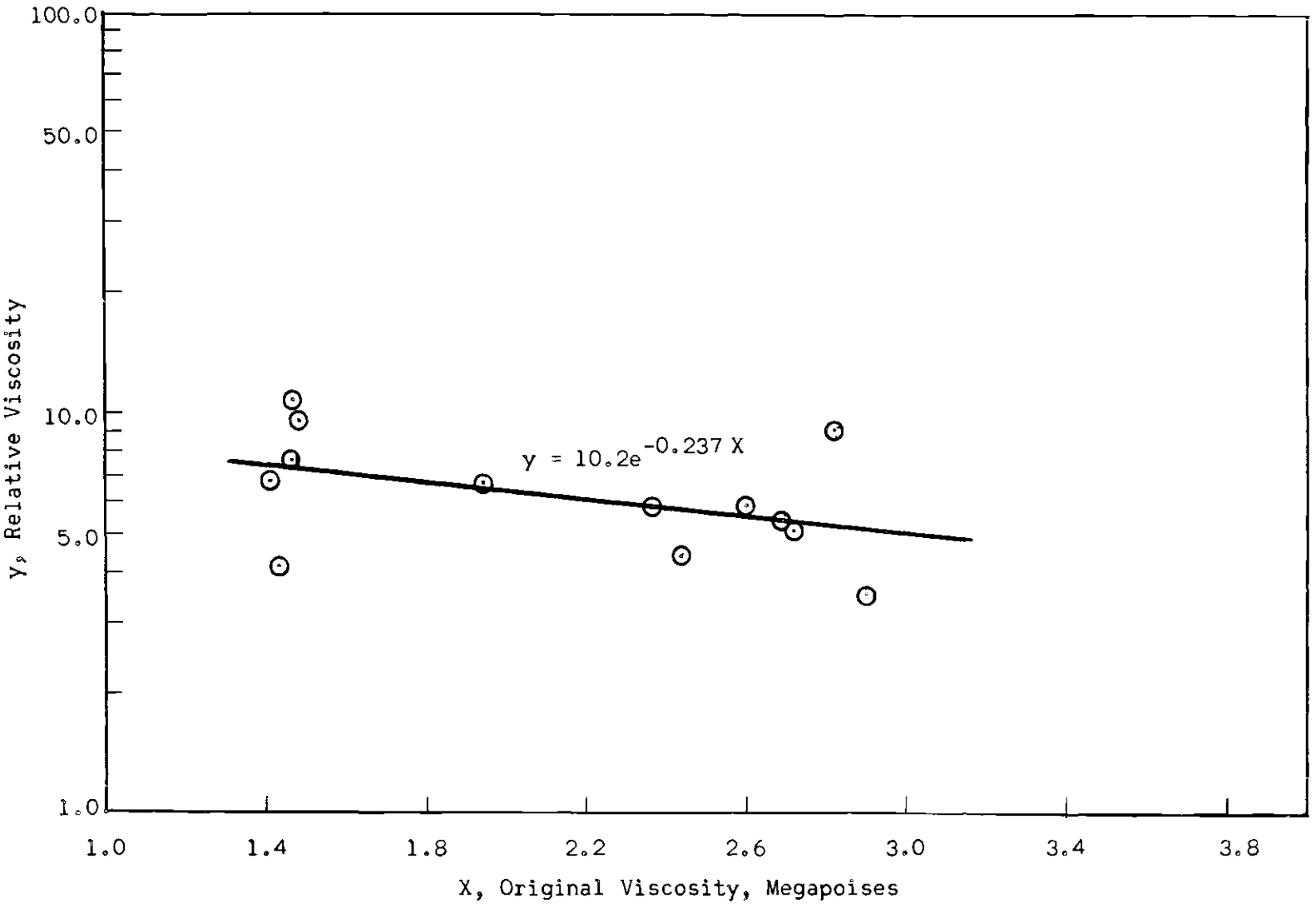

Figure 36. Original Viscosity versus Relative Viscosity for Layer C.

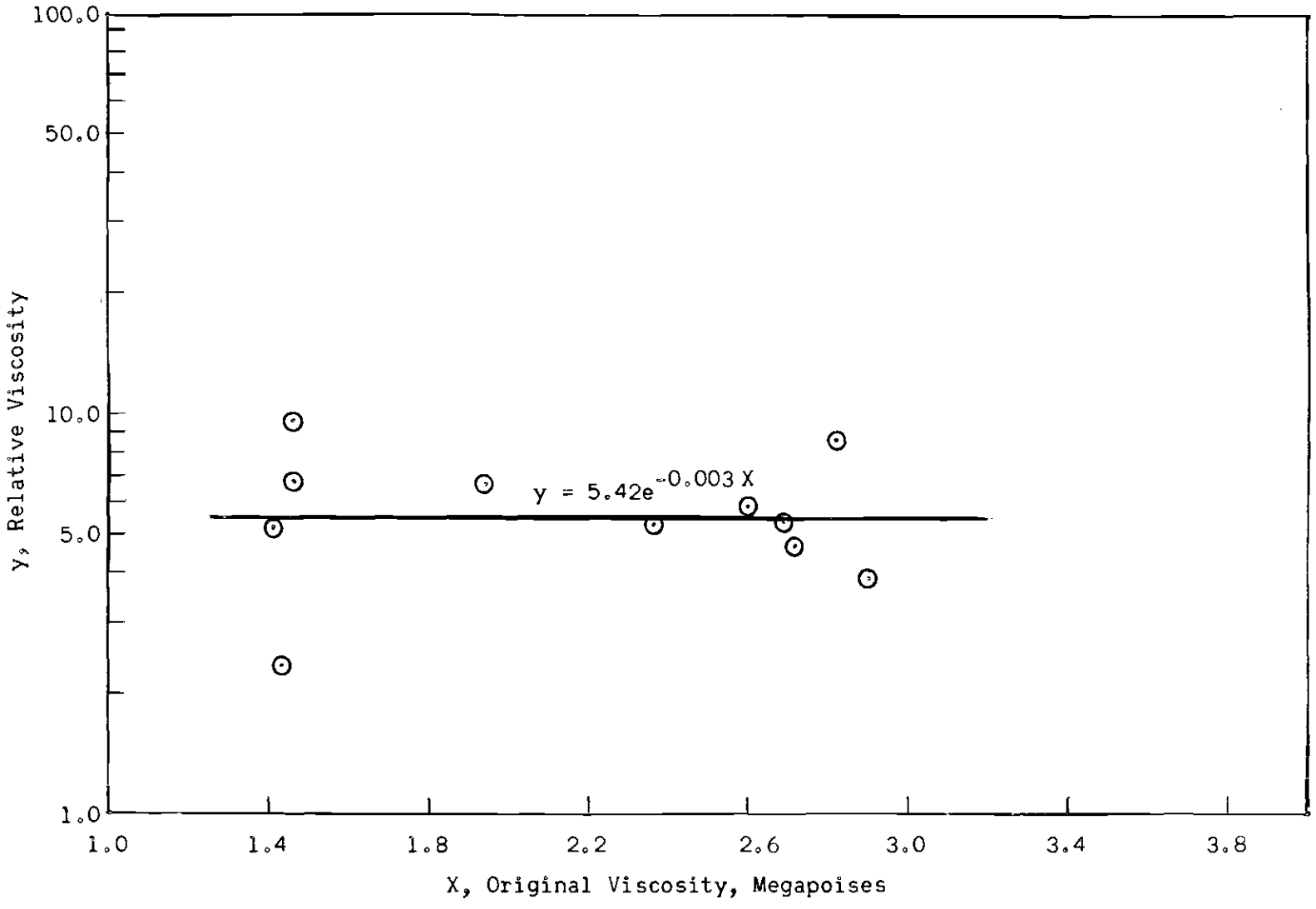

Figure 37. Original Viscosity versus Relative Viscosity for Layer D.

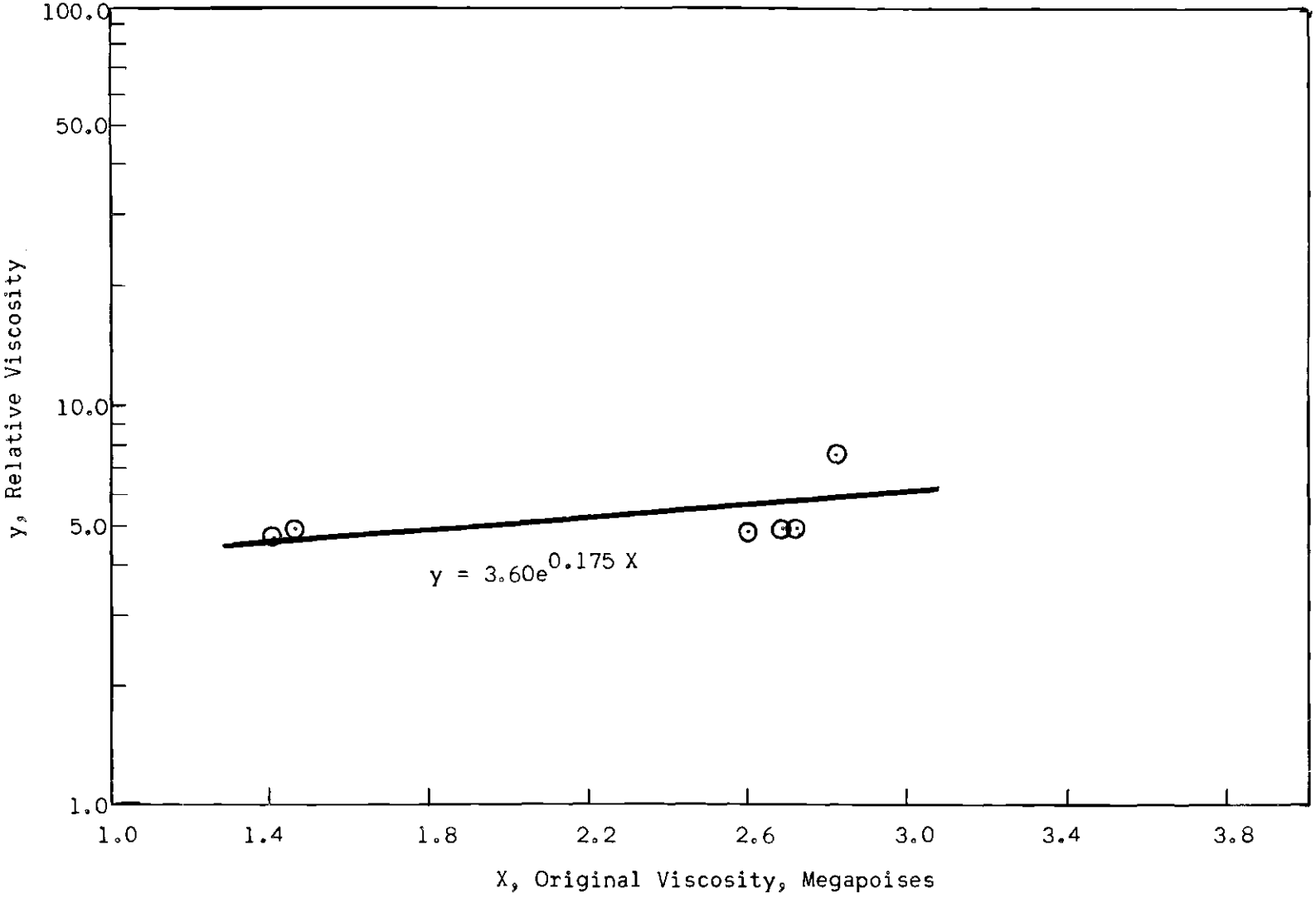

Figure 38. Original Viscosity versus Relative Viscosity for Layer E.

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